U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-257 512

Chemical Characterization of Model Aerosols

Battelle Columbus Labs.

Prepared for

Environmental Sciences Research Lab, Research Triangle Park, N C

Jul 76

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-76-085		

4. TITLE AND SUBTITLE
CHEMICAL CHARACTERIZATION OF MODEL AEROSOLS

5. REPORT DATE
July 1976

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
W.E. Schwartz, G.D. Mendenhall, P.W.Jones, C.J. Riggle, A.P. Graffeo, and D.F. Miller

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Battelle-Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
R801174

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final 6/74 4/76

14. SPONSORING AGENCY CODE
EPA-ORD

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Model aerosols were generated from the individual hydrocarbons, toluene and 1-heptene, by irradiation under simulated atmospheric conditions in the presence of NO_x, or NO_x/SO_2. The reactions were carried out in a 17.3 m^3 environmental chamber. The collected aerosols were subjected to analysis by mass spectrometry and chromatographic techniques, both with and without chemical derivatization. Polyfunctional oxidation products, including quinones and carboxylic acid, were tentatively identified in the toluene aerosol. The 1-heptene filtered aerosol was shown to contain condensation products from different 1-heptene molecules. Tentative identification of a number of vapor-phase species was accomplished in both systems. The health effects of the atmospheric oxidation products from hydrocarbons is discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field Group
*Air pollution *Photochemical		13B
*Toluene reactions		07C
*Heptenes *Chemical analysis		07D
*Aerosols		14B
*Environment Simulation		07E

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	89
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	$5.00/2.25

EPA Form 2220-1 (9-73)

PRICES SUBJECT TO CHANGE

266151

PB 257 512

EPA-600/3-76-065
July 1976

Ecological Research Series

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ECOLOGICAL RESEARCH series. This series describes research on the effects of pollution on humans, plant and animal species, and materials. Problems are assessed for their long- and short-term influences. Investigations include formation, transport, and pathway studies to determine the fate of pollutants and their effects. This work provides the technical basis for setting standards to minimize undesirable changes in living organisms in the aquatic, terrestrial, and atmospheric environments.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/3-76-085
July 1976

CHEMICAL CHARACTERIZATION OF MODEL AEROSOLS

by
W. E. Schwartz, G. D. Mendenhall, P. W. Jones,
C. J. Riggle, A. P. Graffeo, and D. F. Miller
Battelle Memorial Institute
Columbus, Ohio 43201

Grant No. 801174

Project Officer

Ronald K. Patterson
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

Model aerosols were generated from the individual hydrocarbons, toluene and 1-heptene, by irradiation under simulated atmospheric conditions in the presence of NO_x, or NO_x/SO_2. The reactions were carried out in a 17.3 m^3 environmental chamber. The collected aerosols were subjected to analysis by mass spectrometry and chromatographic techniques, both with and without chemical derivatization. Polyfunctional oxidation products, including quinones and carboxylic acid, were tentatively identified in the toluene aerosol. The 1-heptene filtered aerosol was shown to contain condensation products from different 1-heptene molecules. Tentative identification of a number of vapor-phase species was accomplished in both systems. The health effects of the atmospheric oxidation products from hydrocarbons is discussed.

CONTENTS

		Page
ABSTRACT		iii
LIST OF FIGURES		v
LIST OF TABLES		vi
SECTIONS		
I	SUMMARY AND CONCLUSIONS	1
II	INTRODUCTION	2
III	BACKGROUND	3
IV	METHODS AND PROCEDURES	7
	A. Smog Chamber Characteristics	7
	B. Smog-Chamber Cleanup	8
	C. Aerosol Generation, Monitoring and Collection	9
	D. Collection and Analysis of Organic Vapor Samples	11
	E. Preparation of Methyl Esters with Diazomethane	11
V	RESULTS AND DISCUSSION	12
	A. Organic Characterization of Model Aerosols	12
	B. Gas Chromatographic Analysis of Model Aerosols	17
	C. High-Pressure Liquid Chromatography of Derivatized Aerosols	28
	D. Direct Mass Spectral Analysis of Aerosol without Prior Chromatography	29
	E. Infrared Spectrum of 1-Heptene Aerosol	36
	F. Analysis of Vapor Phase Organic Species Associated with Model Aerosols	38
	G. Reaction Types and Mechanisms Inferred from Tentatively Identified Reaction Products in Model Aerosols	44
	H. Health Effects	48
	I. Conclusions	52
REFERENCES		53
APPENDIX A.	METHANE IONIZATION SPECTRA OF COMPOUNDS OBSERVED ON THE GC-MS ANALYSIS (FIGURE 10) OF TOLUENE AEROSOL, DERIVATIZED WITH BSTFA	54
APPENDIX B.	METHANE IONIZATION SPECTRA OF COMPOUNDS TENTATIVELY IDENTIFIED ON THE GC-MS ANALYSIS (FIGURE 15) OF VAPORS ASSOCIATED WITH TOLUENE/NO_x/SO_2 AEROSOLS	61
APPENDIX C.	METHANE IONIZATION SPECTRA OF COMPOUNDS OBSERVED ON THE GC-MS ANALYSIS (FIGURE 16) OF VAPORS ASSOCIATED WITH 1-HEPTENE/NO_x/SO_2 AEROSOLS	73

FIGURES

No.		Page
1	Smog Profile, Toluene/NO_x Aerosol	14
2	Smog Profile, Toluene/NO_x/SO_2 Aerosol	15
3	Smog Profile, 1-Heptene/NO_x/SO_2 Aerosol	16
4	Gas Chromatograms of Methanol Extract of Toluene Aerosol, after Treatment with Diazomethane (Toluene/NO_x)	19
5	Gas Chromatograms of Methanol Extract of Toluene Aerosol, after Treatment with Diazomethane (Toluene/NO_x/SO_2)	20
6	Gas Chromatograms of Methanol Extract of Toluene Aerosol, after Treatment with Diazomethane (Toluene/NO_x/SO_2, exposed to H_2SO_4)	21
7	Gas Chromatograms of Methylene Chloride Extract of Toluene Aerosol, after Treatment with Diazomethane (Toluene/NO_x)	22
8	Gas Chromatograms of Methylene Chloride Extract of Toluene Aerosol, after reatment with Diazomethane (Toluene/NO_x/SO_2)	23
9	Gas Chromatograms of Methylene Chloride Extract of Toluene Aerosol, after Treatment with Diazomethane (Toluene/NO_x/SO_2, exposed to H_2SO_4)	24
10	Reconstructed Gas Chromatograms of Toluene Aerosols Derivatized with BSTFA	26
11	Electron Impact Mass Spectrum of 1-Heptene Aerosol (Sample M599). Successive Spectra Recorded as Probe Temperature Raised from 25 to 200 C	30-32
12	Chemical Ionization Mass Spectrum of 1-Heptene Aerosol (Sample M599). Successive Spectra Recorded as Probe Temperature Raised from 25 to 200 C	33-35
13	Infrared Spectrum of Products in Methylene Chloride. .	37
14	Methane Ionization GC-MS Analysis of Vapor Phase Organic Compounds Associated with Toluene/NO_x Aerosol	41
15	Methane Ionization GC-MS Analysis of Vapor Phase Organic Compounds Associated with Toluene/NO_x/SO_2 Aerosol	42
16	Methane Ionization GC-MS Analysis of Vapor Phase Organic Compounds Associated with 1-Heptene/NO_x/SO_2 Aerosol	43

TABLES

No.		Page
1	Summary of Irradiation Conditions and Smog Parameters	10
2	Solvent Extraction of Model Aerosol Products .	17
3	Sulfur Content of Aerosol Extractable Matter .	27
4	Toxicology of Oxidation Products Obtained from Toluene and 1-Heptene in Smog Chamber Runs	49
5	Components of Embalming Fluid Preparations. . .	51

SECTION 1

SUMMARY AND CONCLUSIONS

This report constitutes the second year's study of the composition of model aerosols from individual hydrocarbon precursors under simulated atmospheric conditions.

In the previous year's work, aerosols derived from toluene, cyclohexene, and α-pinene were examined. Because of the complexity of the products, from α-pinene, research during the present year has concentrated on toluene and the terminal olefin 1-heptene. This pair constitutes a representative aromatic and aliphatic species of the sort found in polluted urban atmospheres.

Aerosols from the systems toluene/NO_x, toluene/NO_x/SO_2, and 1-heptene NO_x/SO_2 were prepared, collected, and subjected to analysis by mass spectral techniques, chemical derivatization, and gas and liquid chromatography. The gas-phase organics associated with the aerosols were also studied. Individual species identified tentatively in toluene aerosol include isomeric hydroxybenzoic acids and hydroxy-p-benzoquinones. Among the gas-phase toluene products were identified tentatively nitrotoluenes, nitrocresols, benzaldehyde, and methyl-p-benzoquinone. The 1-heptene aerosol was examined by mass spectrometry; the results suggested that a number of the components are condensation products of species arising from different 1-heptene molecules. n-Hexaldehyde was tentatively identified among the vapor-phase products from 1-heptene. The possible adverse health effects of aerosol and gas-phase products are suggested to be those arising from a general degradative action toward cellular proteins and amino acids.

SECTION II

INTRODUCTION

This report describes research conducted on "Chemical Characterization Model Aerosols" during the period June 11, 1974 to November 10, 1975. This period constitutes the second project-year under EPA Grant No. 801174. The report detailing results of the first year's study, "Chemical Characterization of Model Aerosols" is available through the National Technical Information Service under NTIS No. PB238557/3.

During the current project period organic analysis of model and atmospheric aerosols was conducted. Model aerosols were generated from individual hydrocarbon precursors under atmospheric simulation in the Battelle-Columbus 17 m^3 environmental chamber.

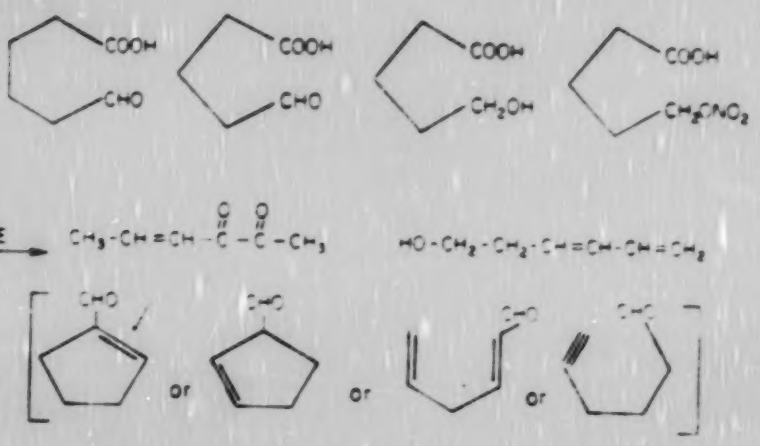
Under the heading below, Background, this year's aerosol characterization studies are placed in perspective with respect to results of the first year's study. Key differences in emphasis and approach are described.

SECTION III

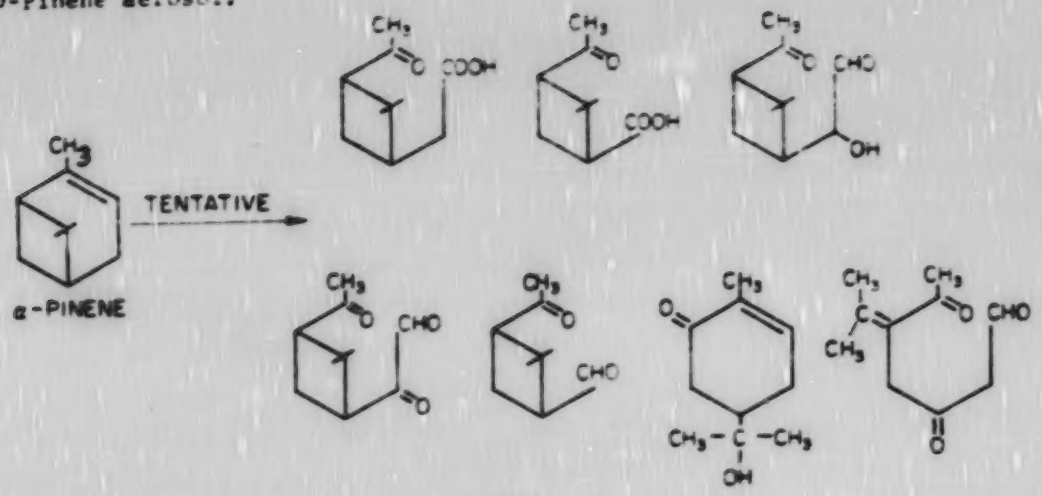
BACKGROUND

During the first year of this program, research was limited to characterization of model aerosols. Three systems were studied; α-pinene/NO_x, toluene/NO_x, and 1-heptene/NO_x. Aerosol generated under atmospheric simulation was collected on glass fiber filters, and organic matter was obtained by solvent extraction. In order to simplify product identification, reaction mixtures were fractionated into defined acid, neutral, and basic components. Products were then analyzed by gas chromatography (GC) and gas chromatography combined with mass spectrometry (GC-MS). Tentative identification of a variety of interesting aerosol products was accomplished. The results of the first year's study are best summarized by reference to these aerosol products. In considering the structures shown below, it should be emphasized that these are tentative identifications.

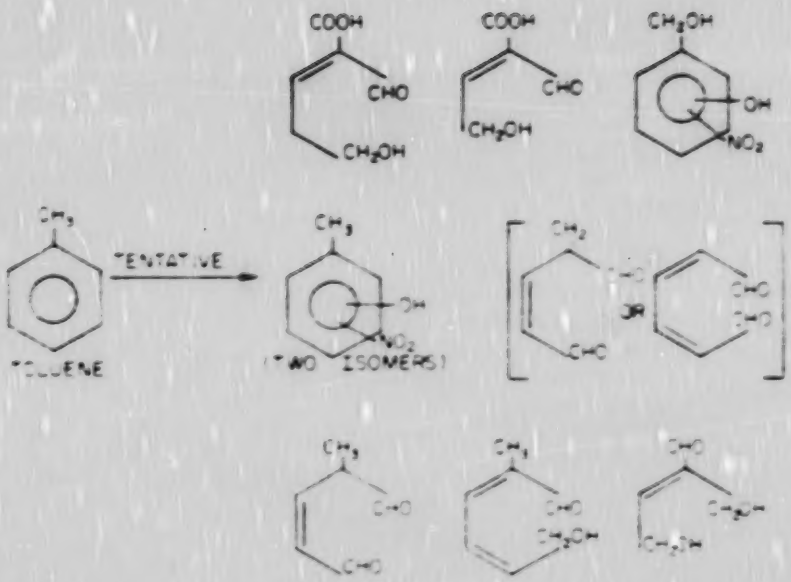
Cyclohexene aerosol.



b-Pinene aerosol.



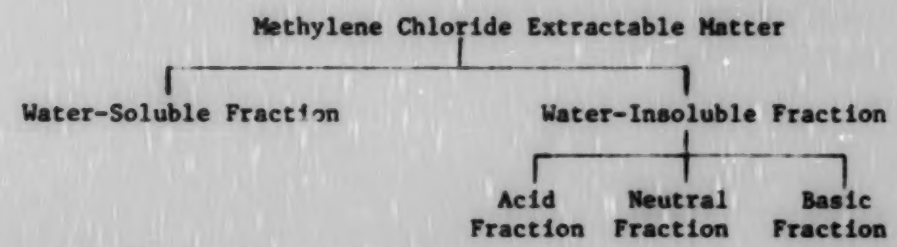
Toluene aerosol.



During the current year's study, we have moved to investigation of simulations including both NO_x and SO_2; specifically, toluene/NO_x/SO_2 and 1-heptene/NO_x/SO_2. In characterizing these systems, the scope of organic analysis has also been broadened. During the first year's effort, the research emphasized identification of aerosol products that had not undergone extensive oxidation or degradation. Identification of such products is profitable in that the structures can be more easily related to the parent hydrocarbon. On the basis of this relationship we may infer the types of reactions occuring under atmospheric simulation. Indeed, in this report we present a discussion of the reaction types and mechanisms suggested by the products identified during the first year's study.

Although identification of the relatively less-degraded aerosol products is helpful in elucidating the nature of aerosol reactions, we have found that such products constitute a rather small fraction of the total organic constituency. Data concerning material distribution was obtained during earlier work on extraction and fractionation of aerosol products. It will be helpful to review this data as well as aspects of the rationale and methods used during the first year of the program.

Collected aerosol was subjected to Soxhlet extraction first with methylene chloride and then with either acetone or methanol. The sequential extraction procedure was used to obtain a measure of the total extractable matter. The methylene chloride extracts were expected to contain products less oxidized than those obtained in methanol or acetone. Hence, consistent with the analytical emphasis and rationale, the methylene chloride extractable matter was used for subsequent fractionation and analysis. Fractionation was conducted according to the scheme below.



The water-insoluble fraction can be expected to contain the relatively less-oxidized, less-degraded components of the reaction mixture. Hence, the water-insoluble material was used for detailed analysis.

Further fractionation into acid, basic, and neutral components was performed by partitioning a methylene chloride solution of the water-insoluble fraction against dilute aqueous acid and then dilute aqueous base. Subsequent analyses could then be conducted on mixtures partly defined according to chemical class. For example, in analyzing a neutral fraction, one might anticipate the presence of aldehydes, ketones, or alcohols, but not carboxylic acids or phenols. This feature of the fractionation approach proved extremely helpful in interpretation of mass spectra of the reaction products.

Data concerning material distribution obtained during the extraction and fractionation steps is shown in Tables B-1 and B-2 (Ref. Report I, p. 26 and p. 29). From the data, it is clear that the water-insoluble fraction of the methylene chloride extractable matter represents only a small fraction of the total solvent extractable matter. In view of this fact, and having achieved some success in characterization of the relatively less-oxidized components of the aerosol products, it was decided to direct future efforts toward a more comprehensive analysis, specifically including the more oxidized components of the reaction mixture.

This decision has had serious consequences as to the experimental approach that may be applied. In particular, the water solubility of the more oxidized products precluded use of the previously applied acid/base/neutral fractionation procedure. Moreover, the extreme polarity of such products severely limited the utility of gas chromatographic analysis. Alternative approaches that have been investigated during the current project period have included selective derivatization followed by high pressure liquid chromatography, and direct examination of aerosols by mass spectral techniques without prior chromatography. Research in these areas will be detailed in sections below.

Finally, mention should be made of an additional area in which the research effort has been broadened. During the current project period collection and analysis of gas-phase organics associated with model aerosols has been conducted. Samples were collected by drawing filtered air through adsorbant traps. Collected organics were later desorbed by heating in a stream of carrier gas and analyzed by GC and GC-MS.

Overall, the program has grown in both the types of aerosol samples included for analysis, and the analytical methods brought to bear on the complex problem of aerosol characterization.

SECTION IV

METHODS AND PROCEDURES

The methods of procedure are those described in the August, 1974, Annual Report on Chemical Characterization of Model Aerosols. The old procedures are partially summarized below along with a description of the new methods.

A. Smog Chamber Characteristics

The smog chamber utilized in these studies is approximately 2.4 m high, 4.9 m long, and 1.5 m wide, having a volume of approximately 17.3 m^3. The surface-to-volume ratio is 0.78. The inside surface consists of 35.3 m^2 of polished aluminum and 9.2 m^2 of FEP-Teflon windows (5 mil thick) through which the reaction mixture is irradiated using an external bank of lamps. The lamp bank consists of 96 fluorescent "black" lamps and 15 fluorescent sunlamps. The spectral distribution of the black lamps peaks in intensity at 370 nm; the sunlamps peak intensity occurs at 310 nm. Light intensity generated corresponds to a k_d of 0.45 min^{-1} as determined by NO_2 photolysis and o-nitrobenzaldehyde actinometry. This intensity is comparable to that of noonday sun over the wavelength integral of NO_2 absorption.

Air supplied to the chamber is taken in through a 15-m stack atop a three-story building, and is passed through a purification system including a permanganate filter bed, a charcoal filter system, an absolute filter, and a humidification unit. After purification, background total-hydrocarbon is generally 1-3 ppmC with the majority of this being methane. A trace of background ethane is occasionally, observed by gas chromatography. Olefins and aromatics have always been below gas chromatographic detection limits. Sulfur dioxide is always below the detection limit of a flame photometric detection (~10 ppb) and carbon monoxide background levels are generally between 1 and 3 ppm as measured by nondispersive infrared spectroscopy. Light scattering readings are essentially the same as for clean air (Raleigh scattering) and the condensation nuclei count is generally less than 200 particles per cubic centimeter.

B. Smog-Chamber Cleanup

Prior to each series of experiments with a different model hydrocarbon, it was necessary to thoroughly clean the chamber's surface to prevent cross contamination of aerosol products. Such cross contamination had been observed during previous studies. Cleanup was accomplished by washing down chamber surfaces with a spray of 4:1 isopropanol:water. Prewashed cloths were used to scrub the surfaces and surgical scrub suits were worn to prevent contamination from street clothing. Throughout the procedure, the chamber was maintained on purge (8500 l min^{-1}). Nevertheless, the high concentration of solvent vapor that develops, requires that the chamber be sealed and that the worker be provided with an auxiliary breathing apparatus.

After cleanup, the chamber was purged overnight and was then permitted to stand with 1 ppm ozone for several hours. Before generation of aerosol for analytical use, a "conditioning" run was conducted using the model system to be studied.

C. Aerosol Generation, Monitoring, and Collection

Detailed data concerning reactant concentrations and conditions are shown in Table 1. After initial concentrations were established, the mixing fan was turned off and irradiation was begun. Parameters monitored throughout the course of the experiment included NO and NO_2 concentration using a continuous Saltzman analyzer, total hydrocarbon concentration using a flame ionization detector, ozone concentration using a chemiluminescence analyzer, and light scattering using an integrating nephelometer.

In general, irradiation was continued until light scattering measurements indicated that maximum aerosol growth had occurred. After this maximum was observed, irradiation was halted and the aerosol was collected by evacuating the chamber contents through tared 10-cm-diameter glass-fiber filters (Gelman Type A) using a high-volume type sampler. Typically, about 11 m^2 of chamber volume was sampled over a 30-minute period. Before use, the filters were washed repeatedly, first with distilled-in-glass methanol, and then with methylene chloride. They were then equilibrated at 50 percent R.H. and tared. After collection, the filters were reequilibrated, weighed, and placed in glass containers for storage at -60°C. After a series of runs was completed, collected aerosol was subjected to Soxhlet extraction, as described in the previous report.

TABLE 1. SUMMARY OF IRRADIATION CONDITIONS AND SMOG PARAMETERS[a]

	Aerosol System		
	Toluene/NO/NO_2	Toluene/NO/NO_2/SO_2	1-Heptene/NO/NO_2/SO_2
Number of runs	6	4	12
Irradiation period, min.	240	240	265
Relative Humidity			
Initial, percent	50	50	50
Final, percent	--	--	38
Hydrocarbon			
Mass irradiated			
Initial concentration, ppm C	73	71	69
Final concertration, ppm C[b]	45	41	6
Nitric oxide			
Initial concentration, ppm	0.97	0.89	1.25
Nitrogen dioxide			
Initial concentration, ppm	0.94	1.09	1.26
Maximum concentration, ppm	1.2	1.5	1.7
Sulfur dioxide			
Initial concentration, ppm	0	1.08	1.0
Final concentration, ppm	0	0.82	0.44
Ozone			
Maximum concentration, ppm	1.1	0.32	0.42
t_{max}, min.	198	200	200
Light scattering			
Maximum, $10^{-4}m^{-1}$	76	120	188
Total aerosol mass collected, mg	11.5[c]	16.3	38.6

(a) Data shown are averages for the series of runs, except for values of total aerosol mass collected, which represent the total mass collected during an entire series of runs.

(b) Includes contribution from products formation.

(c) After treatment with H_2SO_4 aerosol the average weight was 12.9 mg.

D. Collection and Analysis of Organic Vapor Samples

Organic vapor samples associated with model aerosols were collected and subjected to GC-MS analysis. The filtered (pre-extracted tissue quartz) gas sample was drawn through an ambient temperature chromosorb 102 chromatographic trap (15 cm long, 3 cm diameter) at approximately 0.5 cfm by a Gast 0522 pump. Prior to analysis, the traps were sealed with Teflon fittings and protected from light.

The collected samples were subjected to GC-MS analysis by thermally desorbing the collected species at 180°C using a helium flow of approximately 500 ml min^{-1}. The desorbed material was preliminarily transferred to a cooled (-196°C) stainless steel sample loop. Chromatographic injection of the collected sample was subsequently achieved by diverting the GC carrier gas through the cooled sample loop, and simultaneously flash-heating the loop to 250°C, which immediately sweeps the sample to the head of the GC column.(1)* The chromatographic column is routinely interfaced with either a Finnigan 1050 (electron impact) or a Finnigan 3200 (chemical ionization) mass spectrometer; interpretation of electron impact mass spectra is facilitated with a mass spectral matching routine with a data bank of 27,000 spectra.

E. Preparation of Methyl Esters with Diazomethane

An ether solution of diazomethane was prepared from Diazald®, a diazomethane precursor, according to directions given by the supplier (Aldrich). About 1 μg of aerosol, prepared by evaporation of the requisite amount of solution, was dissolved in 1 ml of diazomethane solution and allowed to stand 2-3 hours. The solution was concentrated to a volume of about 0.1 ml. Portions of the concentrate were injected into the gas chromatograph for examination.

---

*References are listed on page 53.

SECTION V

RESULTS AND DISCUSSION

A. Organic Characterization of Model Aerosols

During the current year's study, the following model aerosol systems have been investigated:

- o Toluene/NO_x
- o Toluene/NO_x/SO_2
- o 1-Heptene/NO_x/SO_2

Typical aerosol profiles are shown in Figures 1-3. Irradiation conditions and smog manifestations characterizing the aerosols are further described in Table 1. The values shown in the table represent averages for a series of runs. There was very little run-to-run variation in the parameters; it is considered that the magnitude of such variation was insufficient to be of consequence to the composite aerosol composition.

In addition to generation of the above aerosols, an additional experiment was conducted to determine if any organo-sulfur products are formed after collection of the aerosol by reaction of sulfuric acid with organics residing on the filter. In this experiment, a series of five toluene/NO_x aerosols were generated under conditions described in Table 1. Collected aerosol from four such runs was exposed to sulfuric acid aerosol; one toluene/NO_x sample was retained as a control.

Sulfuric acid aerosol was generated by evaporating a quantity of 98 percent sulfuric acid into the chamber which had been previously humidified to ~50 percent RH. Upon reaching the saturation concentration of sulfuric acid under these conditions ($\sim 10^{-3}$ ppb), nucleation commenced. Aerosol concentration and growth were monitored with a condensation nuclei counter (Environment-One Inc.) and an electrical particle-mobility analyzer (Thermo Systems, Inc.). Aerosol generation was terminated upon reaching a volume concentration of $\sim 700\ \mu m^3/cm^3$. This concentration is approximately equivalent to that expected upon irradiation of 1 ppm SO_2 in a typical smog environment. The mean particle diameter in the volumetric distribution was ~0.2 μm.

To further simulate experimental conditions employed in aerosol generation from toluene/NO_x/SO_2, 1 ppm SO_2 was included during sulfuric acid aerosol generation. Thus the toluene/NO_x aerosol products

were exposed to both sulfuric acid and SO_2. Exposure was conducted as follows. After the sulfuric acid aerosol was fully developed, as described above, portions of the chamber contents were exhausted through filters containing previously collected toluene/NO_x aerosol. Each filter was exposed individually to 15 percent of the chamber contents over a period of 15 minutes.

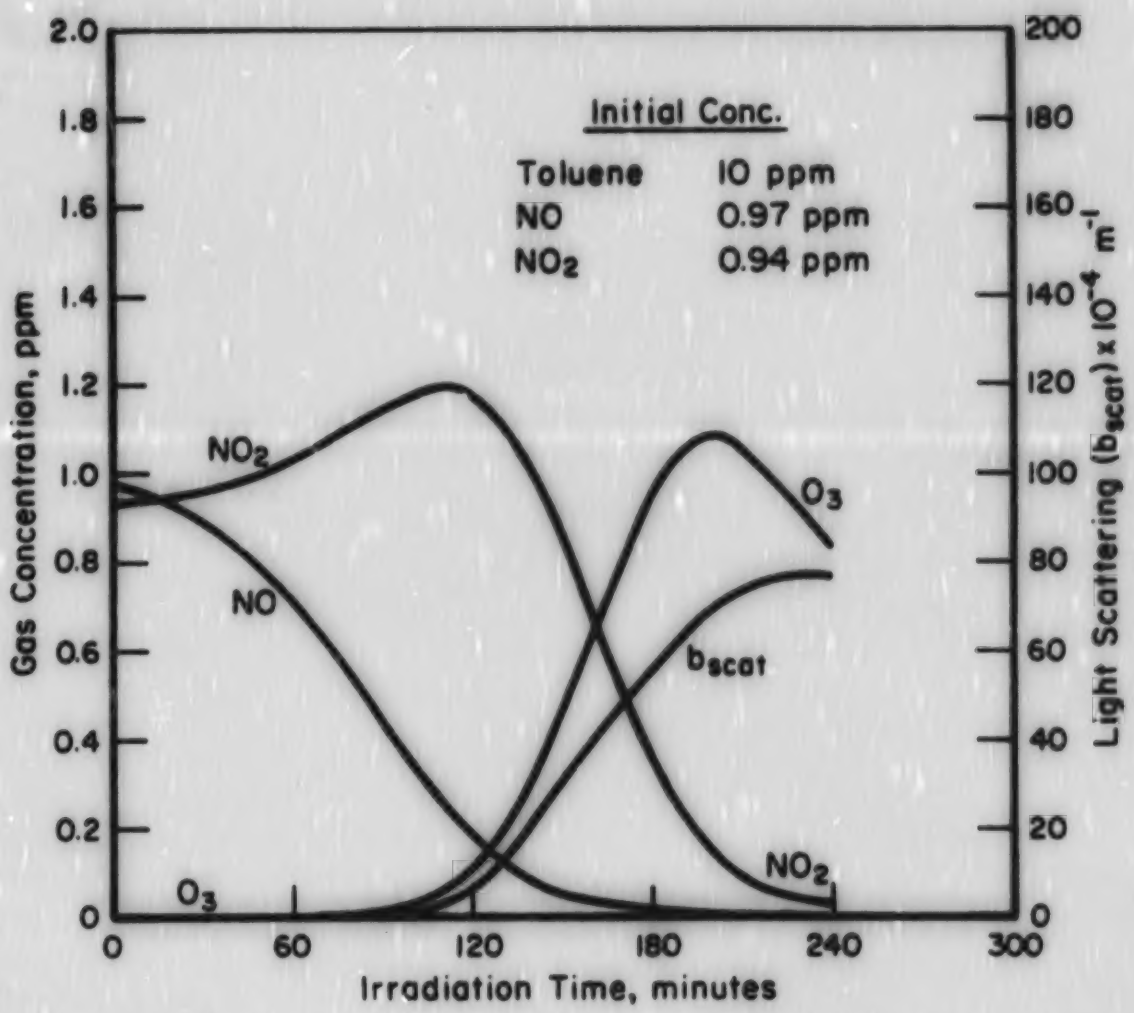


FIGURE 1. SMOG PROFILE, TOLUENE/NO_x AEROSOL

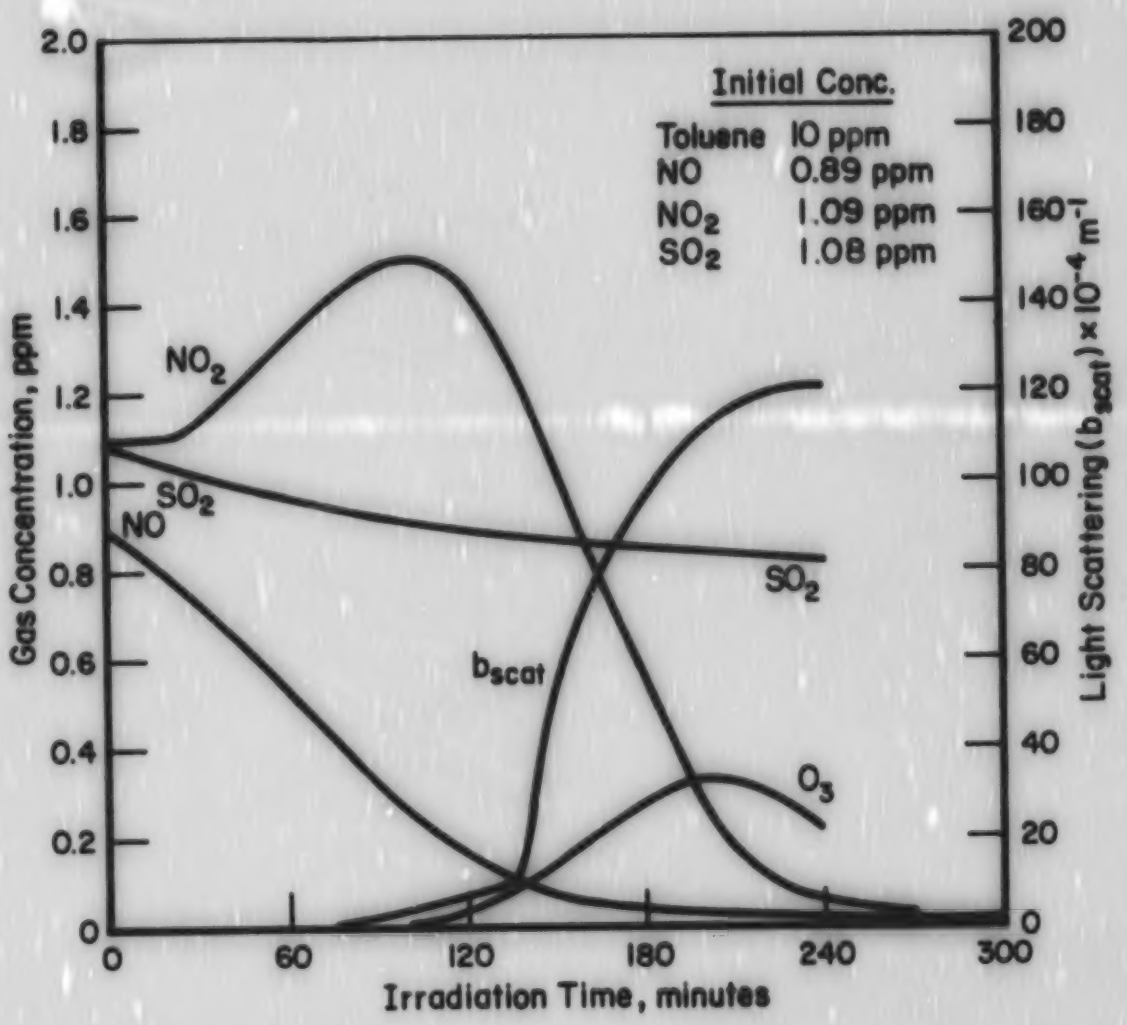


FIGURE 2. SMOG PROFILE, TOLUENE/NO_x/SO_2 AEROSOL

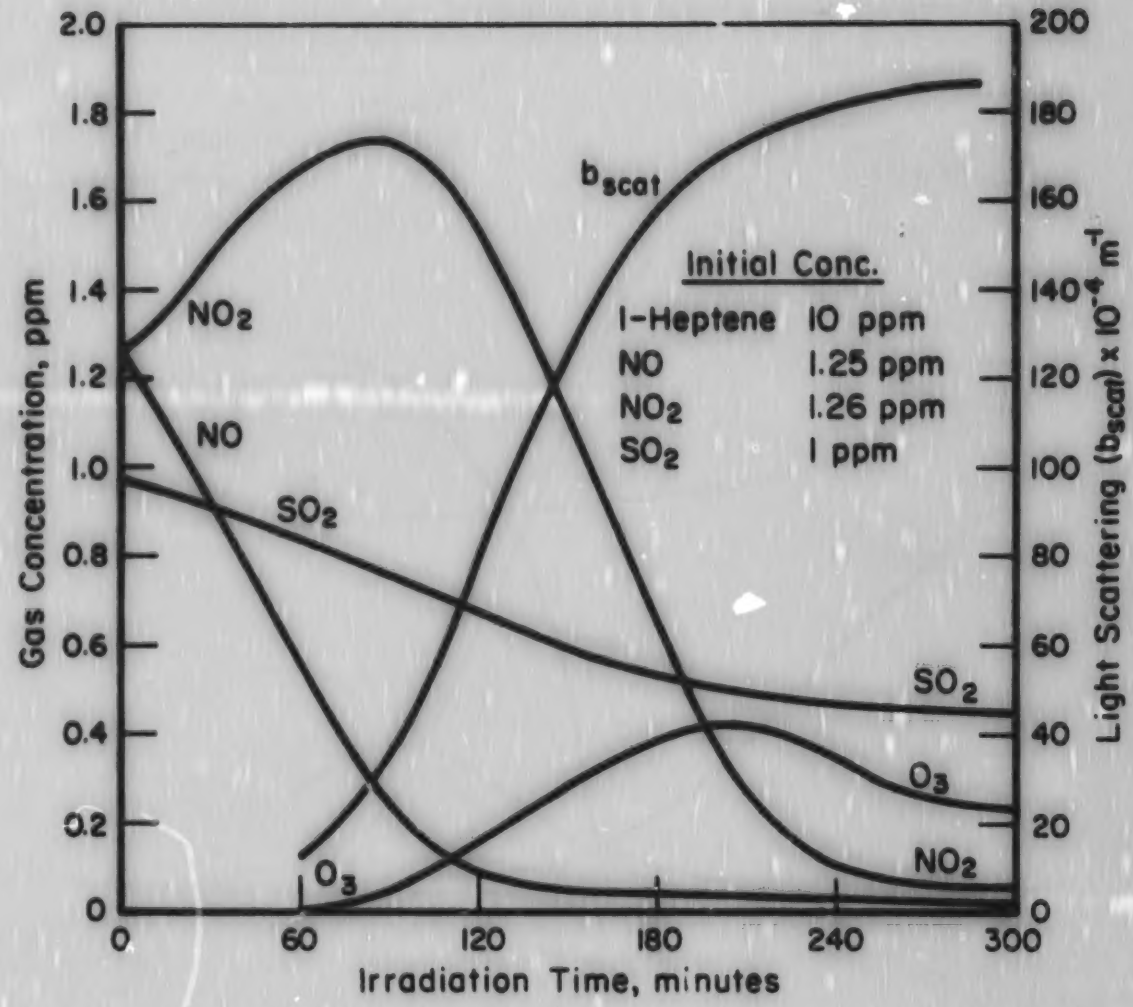


FIGURE 3. SMOG PROFILE, 1-HEPTENE/NO_x/SO_2 AEROSOL

Aerosol products were collected by filtration as described in Methods of Procedure and were then subjected to sequential Soxhlet extraction first with methylene chloride, and then methanol. Values for weight percent solvent extractable are shown in Table 2. Gas-phase organics associated with the model aerosols were collected at the same time as filtration samples by passing filtered chamber contents through Chromsorb 102 adsorbent traps. Aerosol extracts and gas phase organics were analyzed in detail as described under the headings below.

TABLE 2. SOLVENT EXTRACTION OF MODEL AEROSOL PRODUCTS

Aerosol System	Weight-Percent Solvent Extractable	
	First Extraction, Methylene Chloride	Second Extraction, Methanol
Toluene/NO_x aerosol	18	63
Toluene/NO_x aerosol exposed to sulfuric acid aerosol	29	55
Toluene/NO_x/SO_2 aerosol	21	75
1-Heptene/NO_x/SO_2 aerosol	22	49

B. Gas Chromatographic Analysis of Model Aerosols

As described in the Background section of this report, the analytical objectives of this year's research emphasize characterization of the abundant, highly-oxidized components of model aerosol. These polar, water-soluble organics cannot be treated using the previously applied fractionation procedure. Fractionation had proven useful in that particular compound types were isolated in defined fractions. An alternative strategy based on selective derivatization was attempted to distinguish between different compound types. Initial

gas chromatographic analyses were performed on unfractionated, underivated aerosol extracts. It was reasoned that free carboxylic acids, phenols, and other highly polar compounds such as polyols would be entirely retained on the column; only neutral products of moderate polarity would be eluted. A short pre-column can be used to prevent buildup of retained material on the analytical column. The strategy then called for treatment of parallel portions of aerosol extract with:

(a) Diazomethane

(b) O,N-Bis(trimethylsilyl)trifluoroacetamide (BSTFA)

Treatment with diazomethane yields relatively volatile methyl esters from carboxylic and sulfonic acids, and methyl-aryl ethers from phenols. BSTFA reacts with acids and alcohols to form trimethylsilyl (TMS) esters and ethers. Derivatization was first attempted with the aerosol from the toluene runs. Analyses of underivatized methylene chloride and methanol extracts were performed with a 10 ft x 2 mm column of 3-percent OV-17 and a 14 ft x 2 mm column of 3-percent Dexil. The temperature was programmed from 100°C to 275°C at 6 degrees/min. Dual flame-ionization and flame-photometric (sulfur-specific) detectors were employed. The chromatograms obtained showed only a few poorly resolved peaks of negligible intensity. Total detector response suggests that no more than 1 percent of injected matter was eluted (injected samples = 50 µg each). The results suggest that even the non-acid constituents of the aerosol consisted of highly polar products.

Figures 4-9 show several chromatograms obtained after the toluene aerosol extracts were treated with diazomethane. A small increase in total detector response was noted compared to the underivated samples. Nevertheless, the overall response account for less than 10-percent of injected methylene chloride extractable matter and less than 5-percent of injected methanol extractable matter (50 µg injections). The components showing flame-photometric (sulfur) response have been shown in most cases to correspond to impurities in several batches of diazomethane reagent. In the case of the methanol extract of toluene/NO_x/SO_2, two sulfur-containing components appear which may be genuine reaction products. They do not appear in toluene/NO_x aerosol, or toluene/NO_x aerosol exposed to H_2SO_4 aerosol. They account for

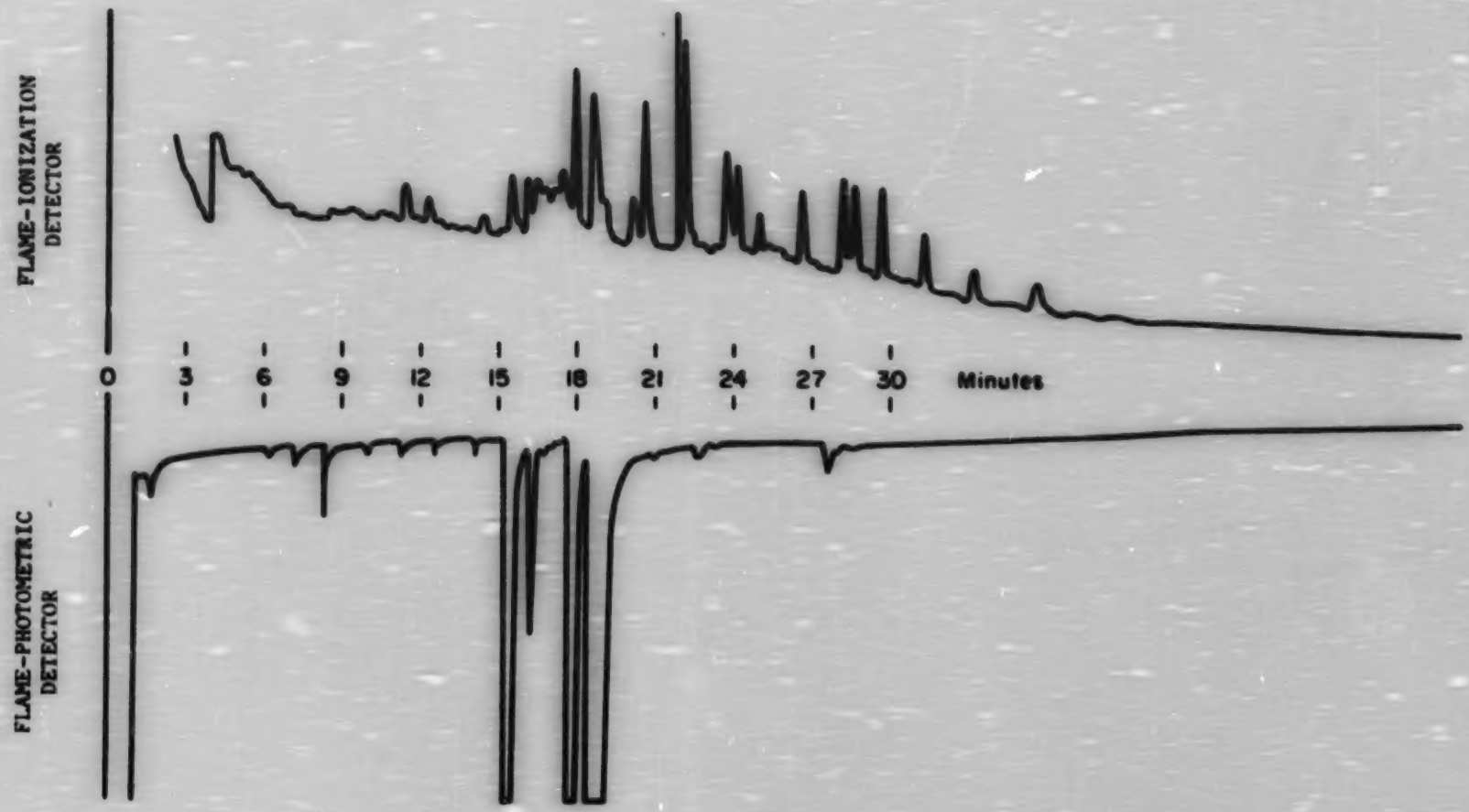


FIGURE 4. GAS CHROMATOGRAMS OF METHANOL EXTRACT OF TOLUENE AEROSOL, AFTER TREATMENT WITH DIAZOMETHANE. SAMPLE M-405. (TOLUENE/NO_x) PROGRAM: 100 C + 6 C/MIN TO 280 C.

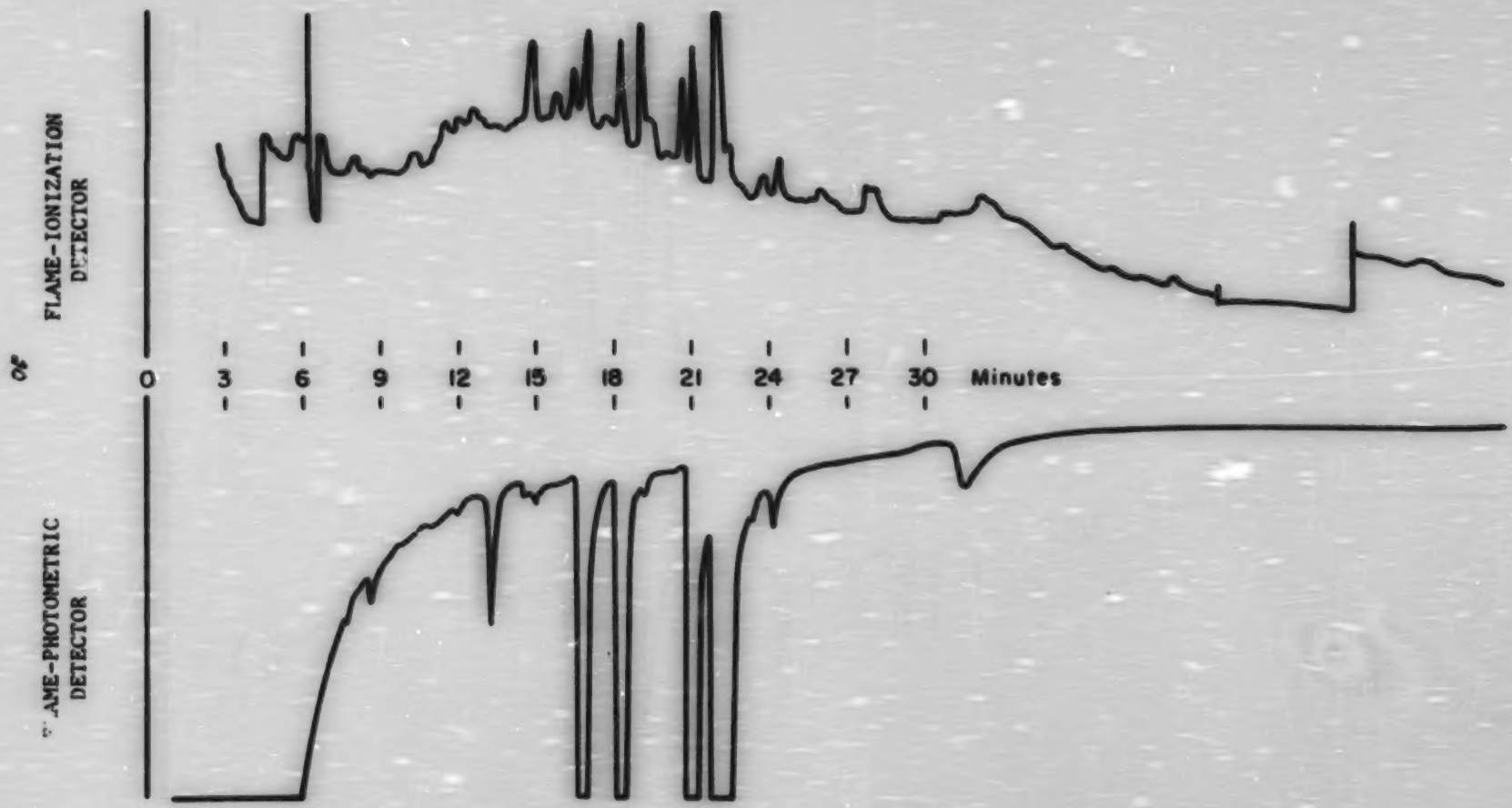


FIGURE 5. GAS CHROMATOGRAMS OF METHANOL EXTRACT OF TOLUENE AEROSOL, AFTER TREATMENT WITH DIAZOMETHANE. SAMPLE M-406-409. (TOLUENE/NO_x/SO_2) PROGRAM: 100 C + 6 C/MIN TO 280 C.

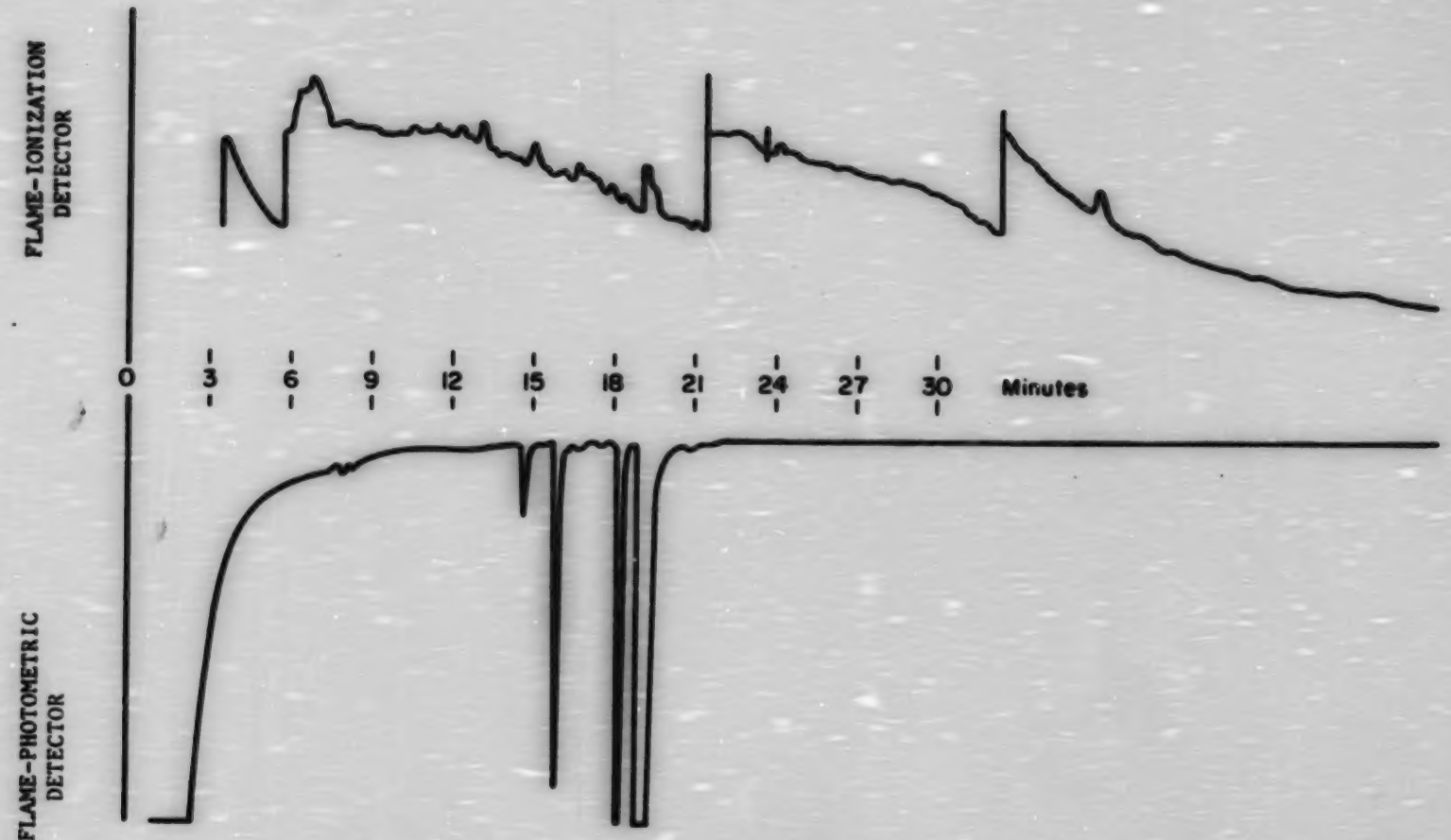


FIGURE 6 . GAS CHROMATOGRAMS OF METHANOL EXTRACT OF TOLUENE AEROSOL, AFTER TREATMENT WITH DIAZOMETHANE. SAMPLE M-401-404. (TOLUENE/NO_x, EXPOSED TO H_2SO_4) PROGRAM: 100 C + 6 C/MIN TO 280 C.

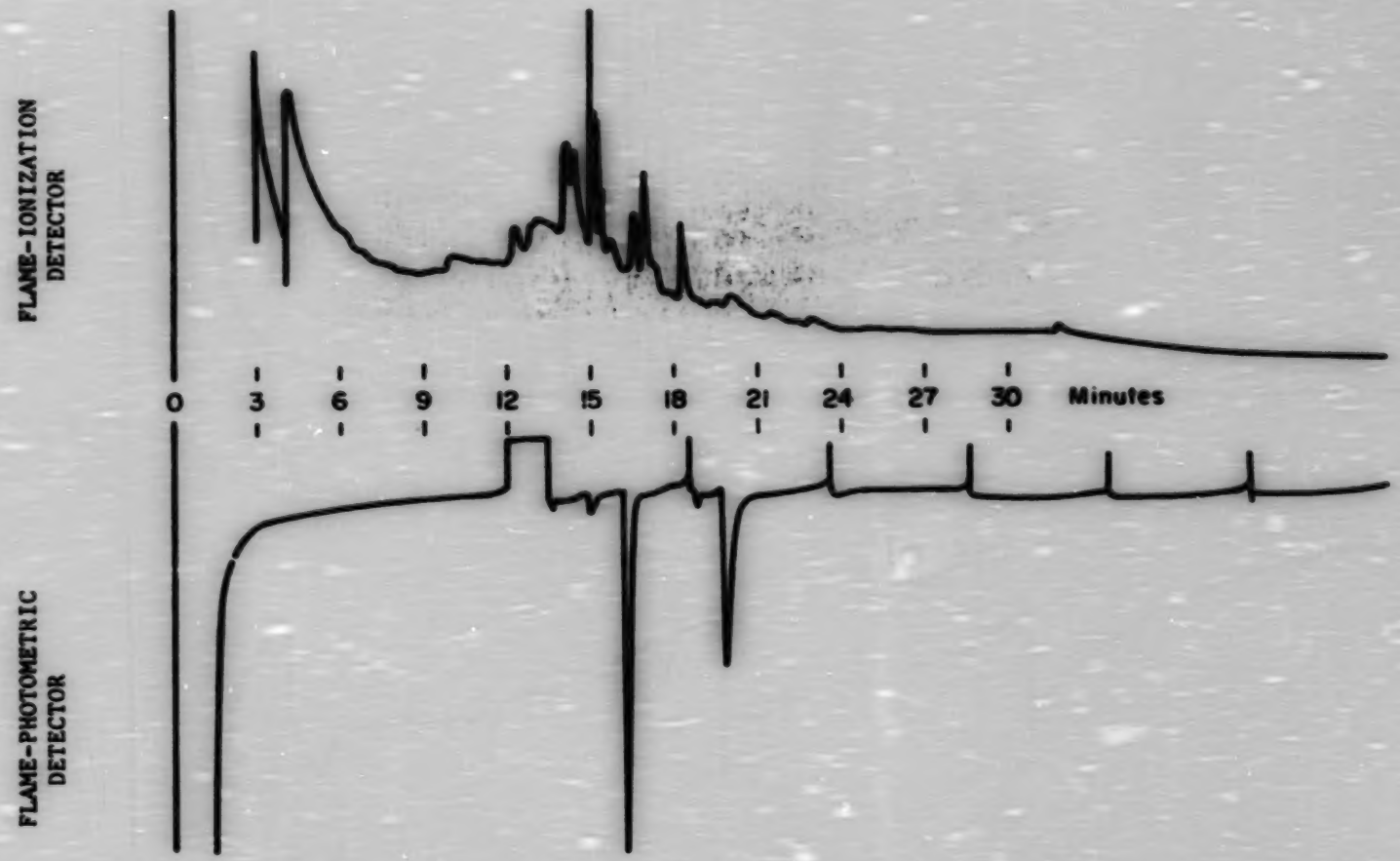


FIGURE 7. GAS CHROMATOGRAMS OF METHYLENE CHLORIDE EXTRACT OF TOLUENE AEROSOL, AFTER TREATMENT WITH DIAZOMETHANE. SAMPLE M-405. (TOLUENE/NO_x) PROGRAM: 100°C + 6 C/MIN TO 280 C.

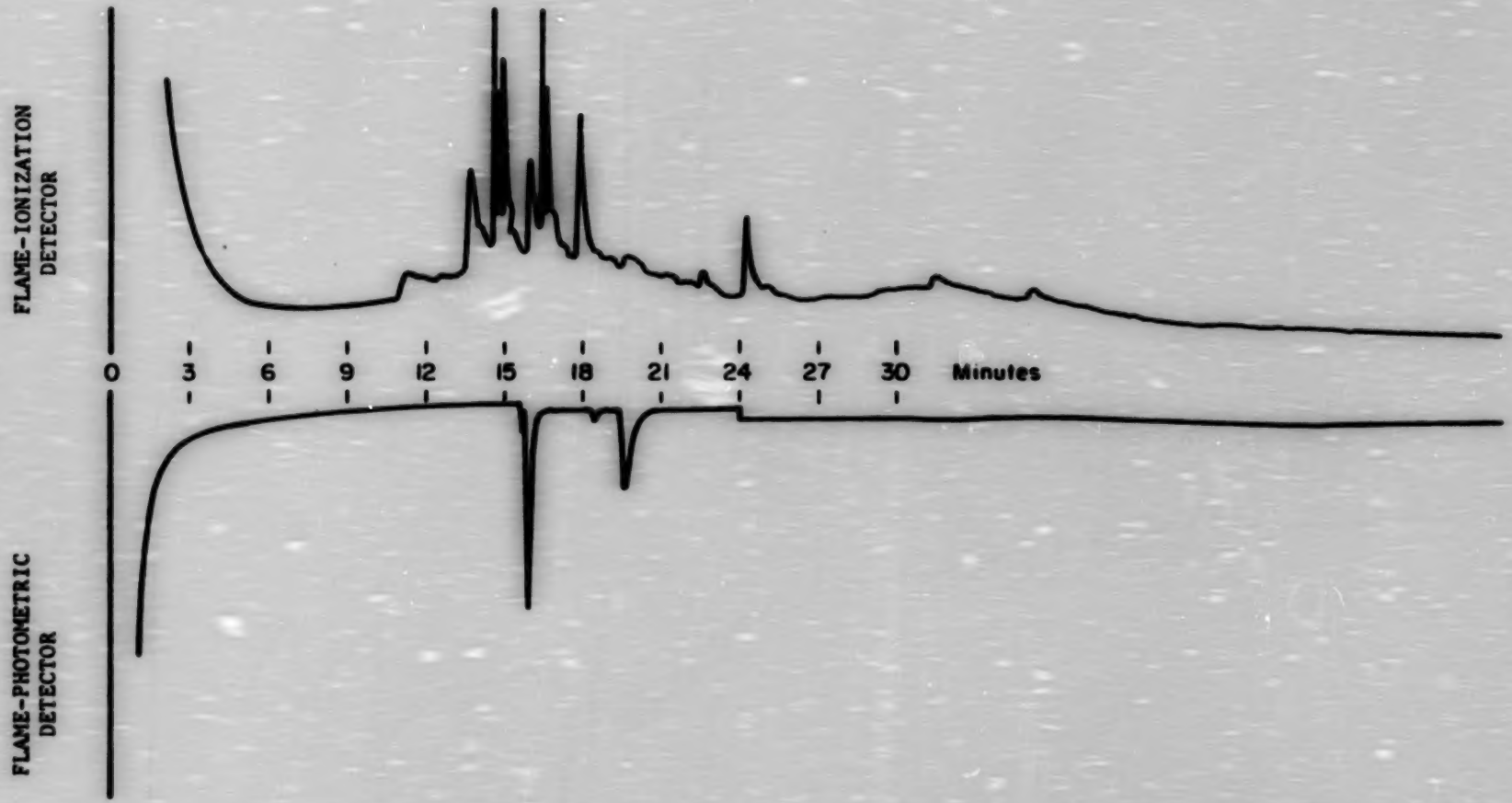


FIGURE 8. GAS CHROMATOGRAMS OF METHYLENE CHLORIDE EXTRACT OF TOLUENE AEROSOL, AFTER TREATMENT WITH DIAZOMETHANE. SAMPLE M-406-409. (TOLUENE/NO_x/SO_2) PROGRAM: 100 C + 6 C/MIN TO 280 C.

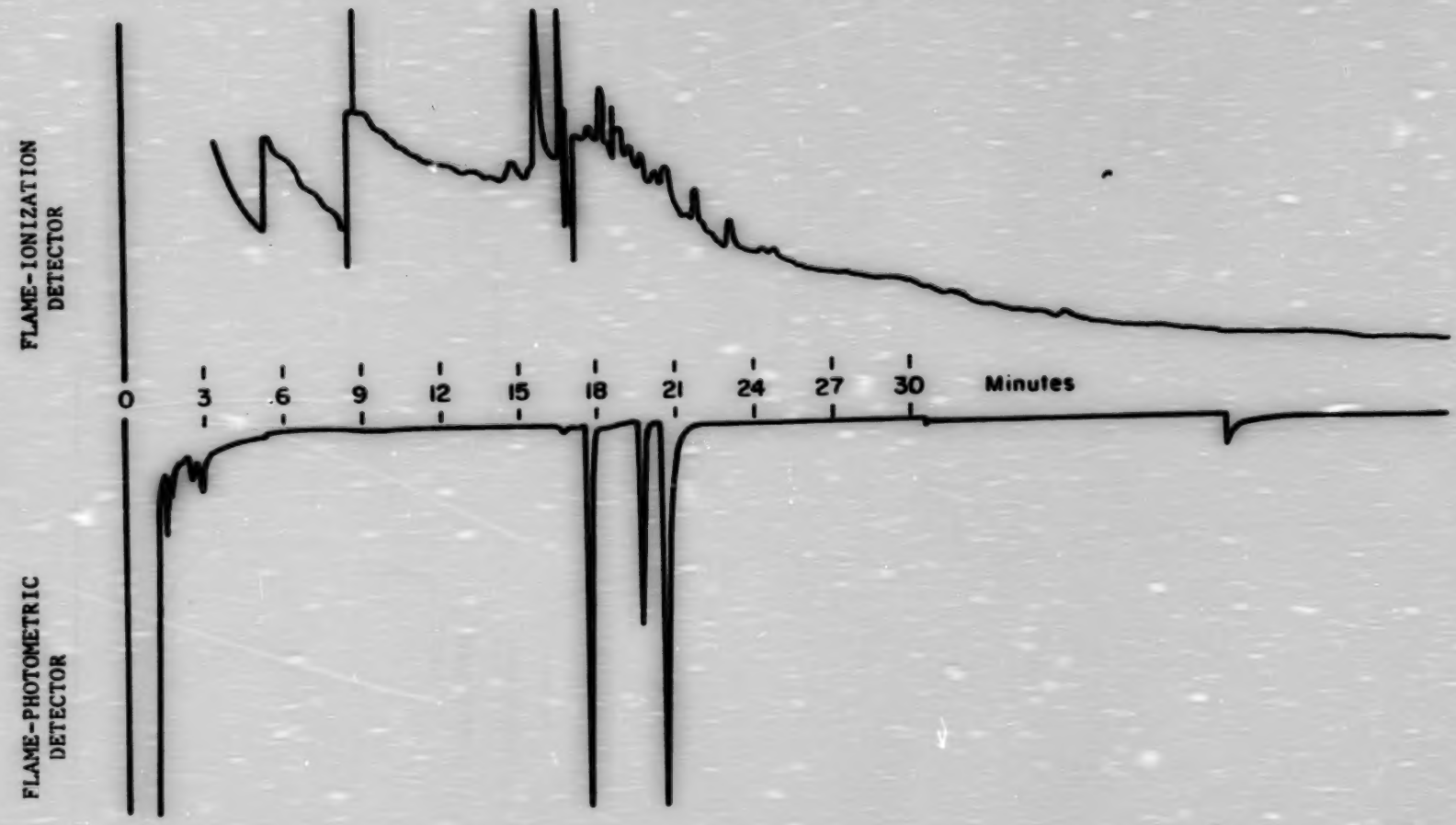


FIGURE 9. GAS CHROMATOGRAMS OF METHYLENE CHLORIDE EXTRACT OF TOLUENE AEROSOL, AFTER TREATMENT WITH DIAZOMETHANE. SAMPLE M-401-404, (TOLUENE/NO_x EXPOSED TO H_2SO_4) PROGRAM: 100 C + 6 C/MIN TO 280 C.

less than 1-percent of the injected sample, however.

Comparison of chromatograms for diazomethane treated extracts of the three toluene aerosols suggest that exposure of collected toluene/NO_x aerosol products to sulfuric acid aerosol does not lead to formation of new products (detectable by this approach). In the diazomethane-treated, methylene chloride extractable matter from toluene/NO_x/SO_2 aerosol there is only one moderate peak not observed in the corresponding sample of toluene/NO_x aerosol (peak at 25 minutes).

As described above, the next step in the analytical approach called for derivatization with BSTFA. It was reasoned, that if the uneluted material consisted of non-volatile alcohols or polyols, BSTFA should generate volatile TMS ethers. Gas chromatographic analysis of toluene aerosol products indicates that a significantly larger fraction of subjected material is being eluted after BSTFA treatment (~30-percent eluted). Thus, these samples were analyzed by GC-MS. Reconstructed gas chromatograms are shown in Figure 10.

The CI-MS spectra of the BSTFA-derivatized samples are shown in Appendix A. Most of the spectra, even after background subtraction, showed numerous peaks, and only the relatively simple spectra that appeared to contain only one major component have been included. In those cases the parent ions were identified and structures were assigned by selection of reasonable structures with the correct molecular weights. The compounds tentatively identified are shown in the figure. We emphasize the tentative nature of these assignments.

The methylene chloride extract of 1-heptene aerosol was similarly treated with BSTFA and analyzed gas chromatographically. Total detector response corresponded to only 5-percent of injected material. Thus, the sample was not analyzed by GC-MS.

For both 1-heptene and toluene aerosols analysis by flame photometric gas chromatography revealed negligible sulfur response above blank. In view of the low sulfur response for all aerosol samples, extracts were subjected to analyses for total sulfur. The data are shown in Table 3. Samples taken for analysis varied somewhat in size, leading to some variation in the lower limit of detection. Thus, any

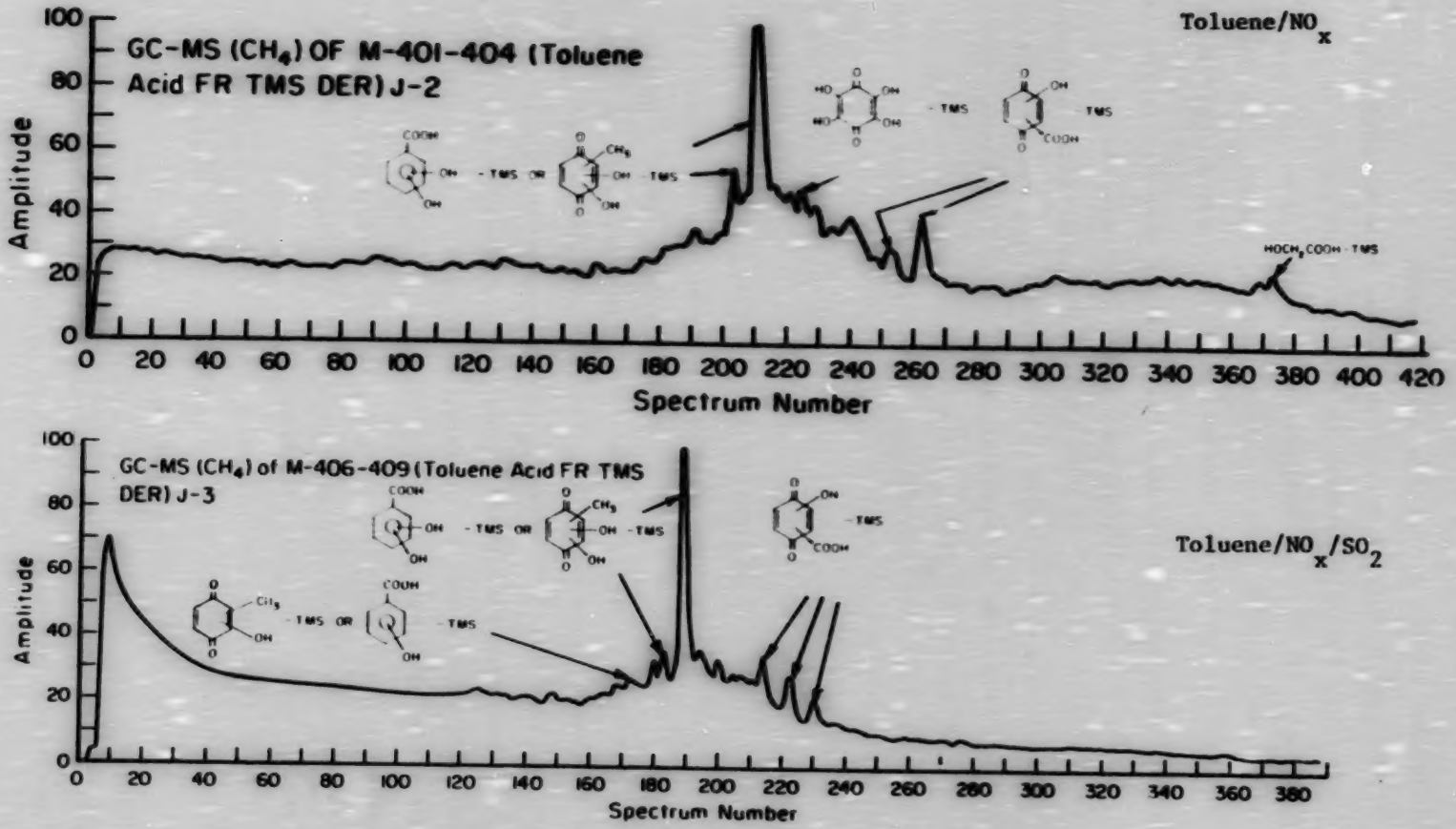


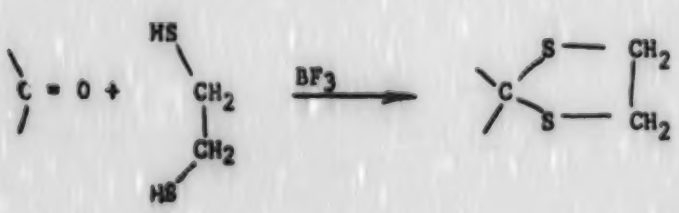
FIGURE 10. RECONSTRUCTED GAS CHROMATOGRAMS OF TOLUENE AEROSOLS DERIVATIZED WITH BSTFA

values below 1-percent sulfur should be viewed as approximately equivalent. The methanol extracts for toluene/NO_x/SO_2 aerosol and toluene/NO_x exposed to sulfuric acid aerosol show significantly higher concentrations of sulfur, which probably arise from inorganic sulfate soluble in the methanol. This was indicated by a sulfate analysis of one collected aerosol from a 1-heptene/NO_x/SO_2 run, which showed 40% of $SO_4^=$ by weight of total particulates on the filter. These data indicate that the low concentrations of organo-sulfur compounds observed by flame-photometric gas chromatography was not due to retention of abundant organo-sulfur compounds on the column.

TABLE 3. SULFUR CONTENT OF AEROSOL EXTRACTABLE MATTER

Aerosol System	Weight-Percent Sulfur	
	Methylene Chloride Extractable Matter	Methanol Extractable Matter
Toluene/NO_x aerosol	<0.5	<0.3
Toluene/NO_x/SO_2 aerosol	<0.8	3.9
Toluene/NO_x aerosol exposed to sulfuric acid aerosol	<0.8	1.2
1-Heptene/NO_x/SO_2 aerosol	0.1	17.9

One additional derivatization approach was attempted to facilitate gas chromatographic analysis. It has been observed that low molecular weight aldehydes and ketones tend to polymerize at the elevated temperatures of gas chromatographic analysis. In order to determine whether such compounds correspond to the uneluted fraction of aerosol products, extractable matter was treated with ethanedithiol to stabilize such carbonyls as dithiolane derivatives.



Preparation of dithiolane derivatives is additionally useful in that the derivatives give both flame-ionization and flame-photometric response. In these analyses, a rather high blank was obtained. Nevertheless, for both toluene and 1-heptene aerosols no significant components above blank were observed. Based on the sample size taken for derivatization, injected material should correspond to 20 μg. Virtually complete loss of sample to the aqueous phase during workup could account for chromatographic results observed.

Results of the series of gas chromatographic analyses suggests that the aerosol products consist principally of highly oxidized, highly polar compounds. These have not been rendered volatile by generally employed derivatization techniques. In view of the failure of this approach, two different techniques have been investigated to determine feasibility. These are:

(1) High-pressure liquid chromatography followed by mass spectrometric analyses of isolated products.

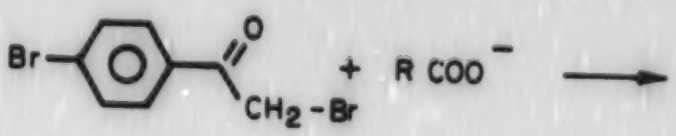
(2) Direct mass spectral analysis of aerosol without chromatography.

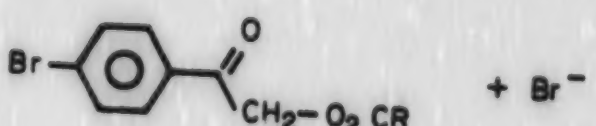
These studies are described under subsequent headings.

C. High-Pressure Liquid Chromatography of Derivatized Aerosols.

Since the functional groups expected in the components of the aerosol do not absorb light strongly, the UV-visible detection system currently in use with the HPLC instrument was not suitable for analysis of small amounts of atmospheric aerosols. Simple derivatives of the components are suitable, however, if the derivatizing reagent contains an absorbing group.

Priliminary experiments were carried out with a sample of the 1-heptene aerosol. The derivatizing reagent was α,p-dibromoacetophenone, which reacts with acids as follows:



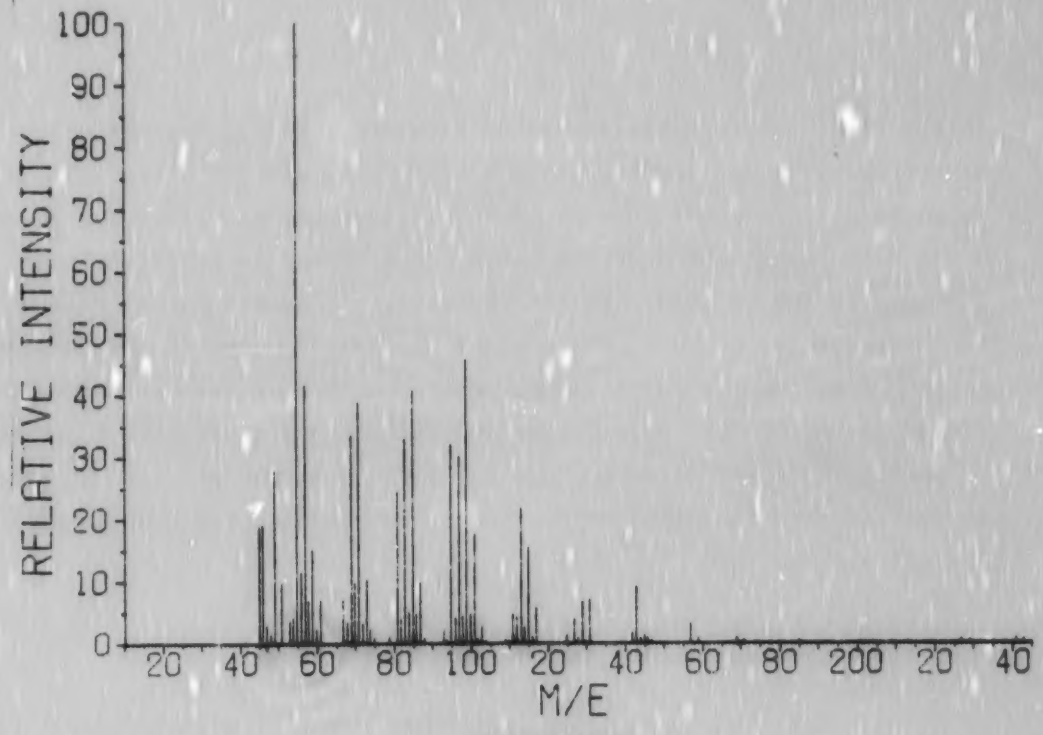


This reagent was repeatedly reacted with the methanol extract of the 1-heptene aerosol and chromatographed using HPLC with UV detection. A large peak corresponding to the derivatizing reagent was always observed. Other peaks were also observed but did not appear on duplicate runs. This may be due to impurities in the derivatizing reagent as well as to interferences by some component of the sample. Due to the unknown nature of the sample and the experimental nature of derivatization reactions in HPLC, more development in optimizing derivatization procedures is needed. These include methods for derivatization of alcohol, ketone, as well as acid functionalities, and of compounds containing multiple functionalities.

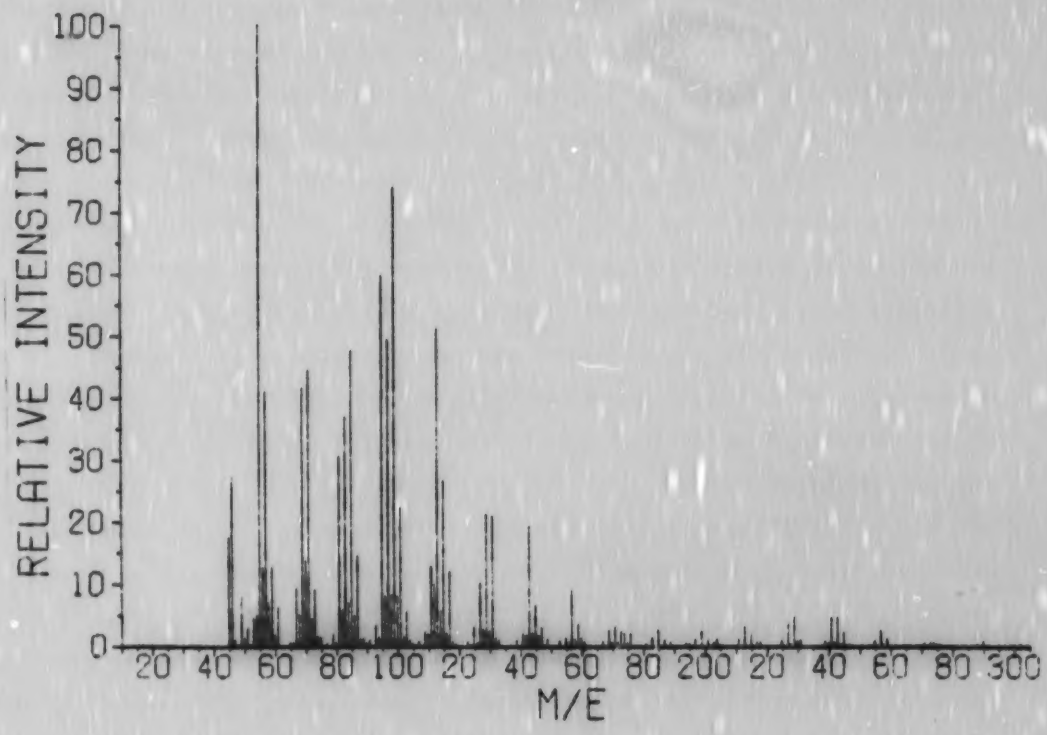
D. Direct Mass Spectral Analysis of Aerosol without Prior Chromatography.

Since the bulk of the 1-heptene aerosol products did not pass through a chromatographic column under our conditions, even when derivatized, we examined a sample of 1-heptene aerosol that was evaporated from a solution placed directly on the probe of the mass spectrometer. The probe was placed in the instrument and heated while successive spectra were run. The procedure was carried out twice, first with conventional electron impact (EI) and then with chemical ionization (CI) by proton transfer from $C_4H_{10}^+$ ion. Under these conditions, we expect low-molecular weight species to volatilize first, followed by higher molecular weight species with lower vapor pressures. The resulting spectra (Figures 11 and 12) are, of course, complicated because the method does not cleanly separate related compounds, and because a signal at any given m/e value can result from several isomeric compounds present in the sample.

The EI spectra (Figure 11) show fragments up to about 260, which corresponds approximately to two heptene molecules plus four oxygens $(C_7H_{14}O_2)_2 = 260$. The CI spectra (Figure 12) show more distinctive features, in part because CI usually gives simpler fragmentation patterns and larger parent ions. Spectrum No. 4 shows two groups of peaks with a minimum around m/e 180, while spectrum No. 7 has a second minimum around m/e 300. Each group of peaks consists of triplets of quartets separated by 14-16 mass units. This mass difference is equal

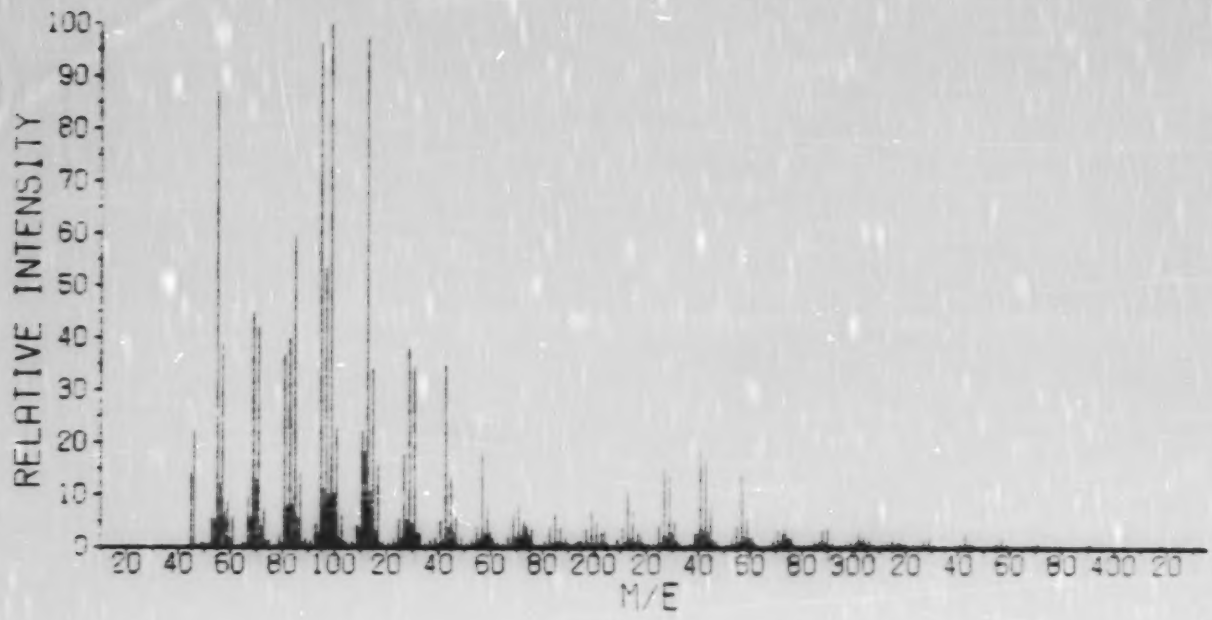


SPECTRUM NO. 2

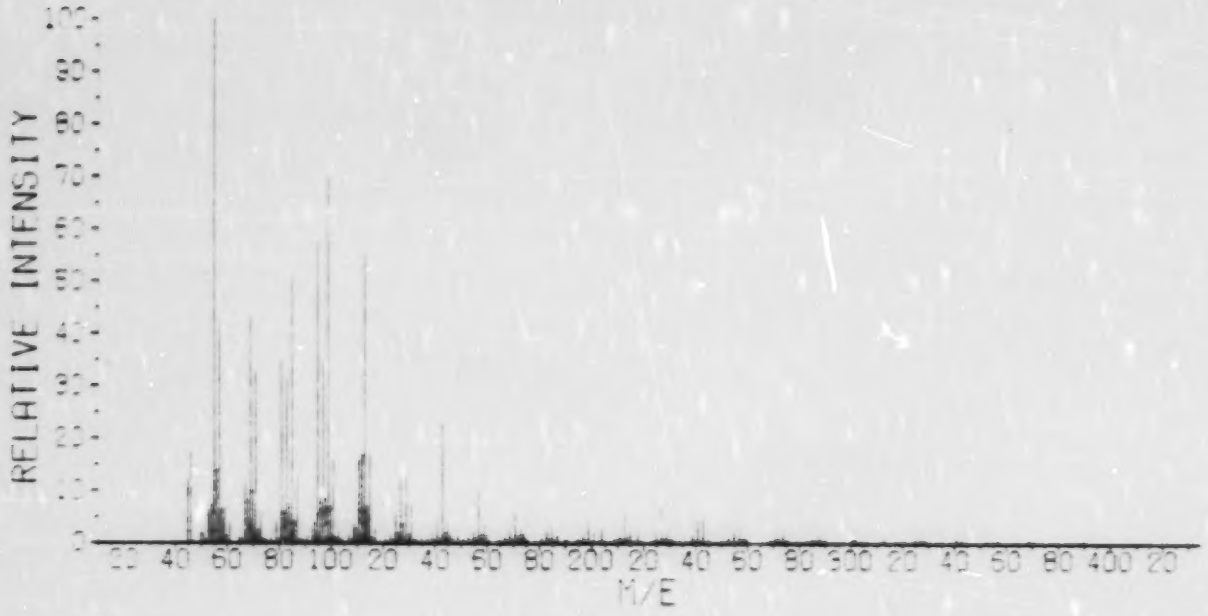


SPECTRUM NO. 3

FIGURE 11. ELECTRON IMPACT MASS SPECTRUM OF 1-HEPTENE AEROSOL (SAMPLE M599). SUCCESSIVE SPECTRA RECORDED AS PROBE TEMPERATURE RAISED FROM 25 TO 200 C.

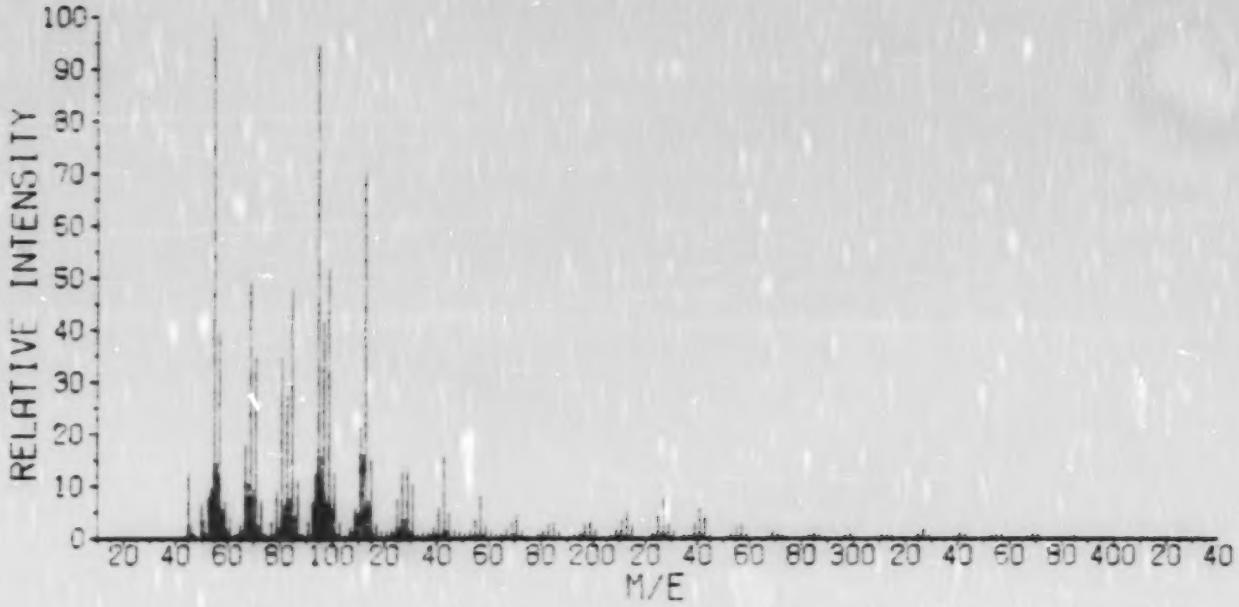


SPECTRUM NO. 4

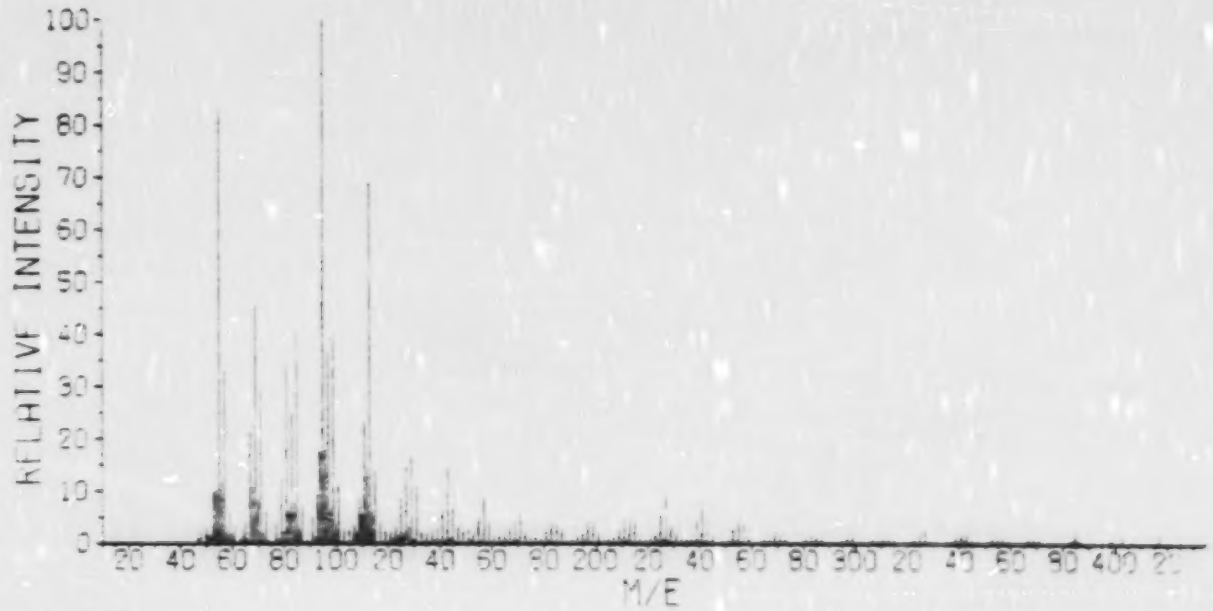


SPECTRUM NO. 5

FIGURE 11. ELECTRON IMPACT MASS SPECTRUM OF 1-HEPTENE AEROSOL (SAMPLE M599). SUCCESSIVE SPECTRA RECORDED AS PROBE TEMPERATURE RAISED FROM 25 TO 200 C.

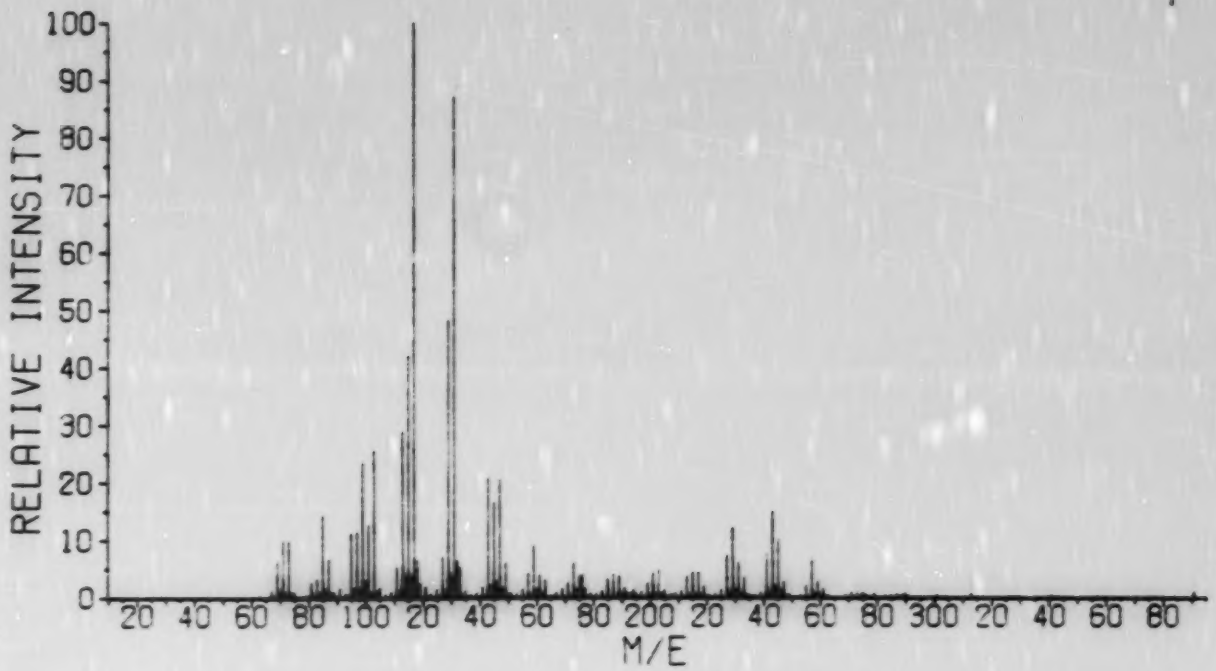


SPECTRUM NO. 7

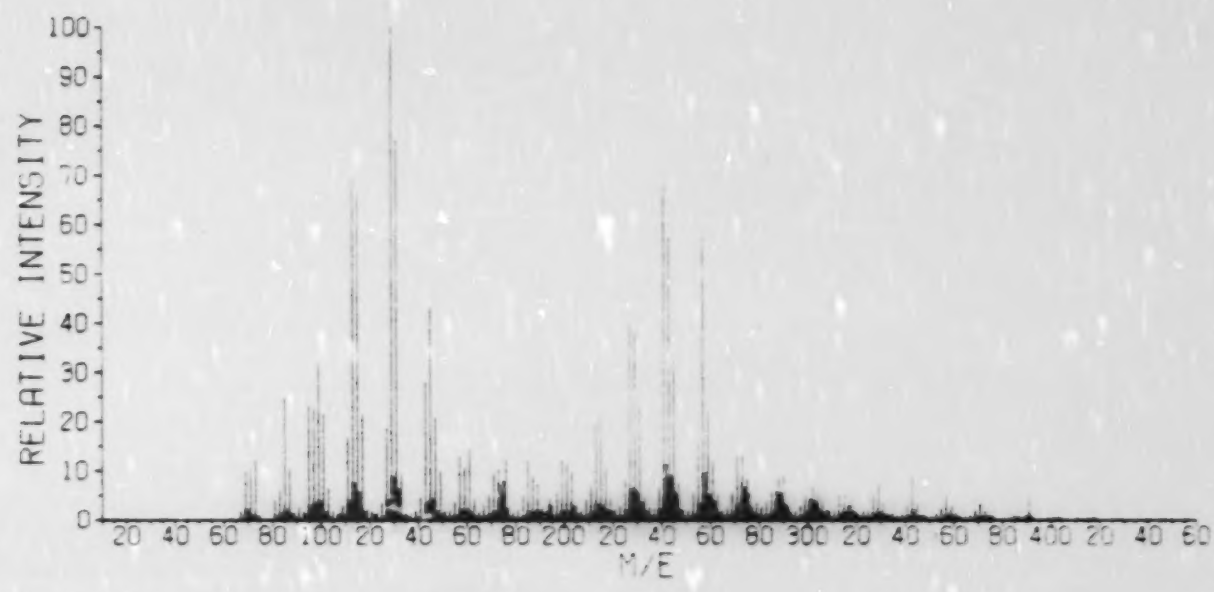


SPECTRUM NO. 8

FIGURE 11. ELECTRON IMPACT MASS SPECTRUM OF 1-HEPTENE AEROSOL (SAMPLE M599). SUCCESSIVE SPECTRA RECORDED AS PROBE TEMPERATURE RAISED FROM 25 TO 200 C.

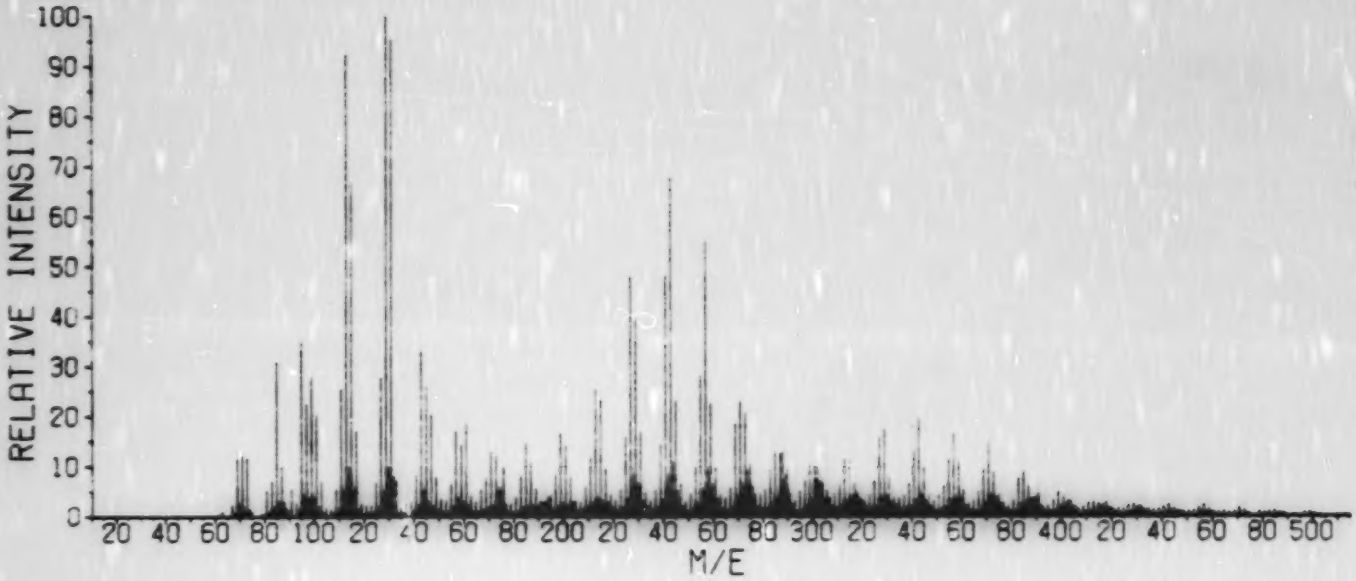


SPECTRUM No. 1

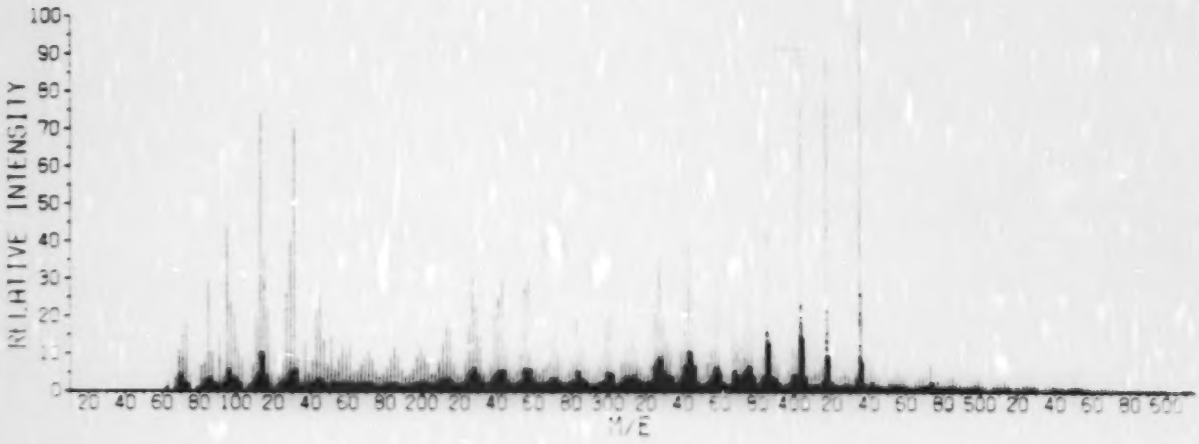


SPECTRUM NO. 4

FIGURE 12. CHEMICAL IONIZATION MASS SPECTRUM OF 1-HEPTENE AEROSOL (SAMPLE M599). SUCCESSIVE SPECTRA RECORDED AS PROBE TEMPERATURE RAISED FROM 25 TO 200 C.



SPECTRUM NO. 7



SPECTRUM NO. 10

FIGURE 12. CHEMICAL IONIZATION MASS SPECTRUM OF 1-HEPTENE AEROSOL (SAMPLE M599). SUCCESSIVE SPECTRA RECORDED AS PROBE TEMPERATURE RAISED FROM 25 TO 200 C.

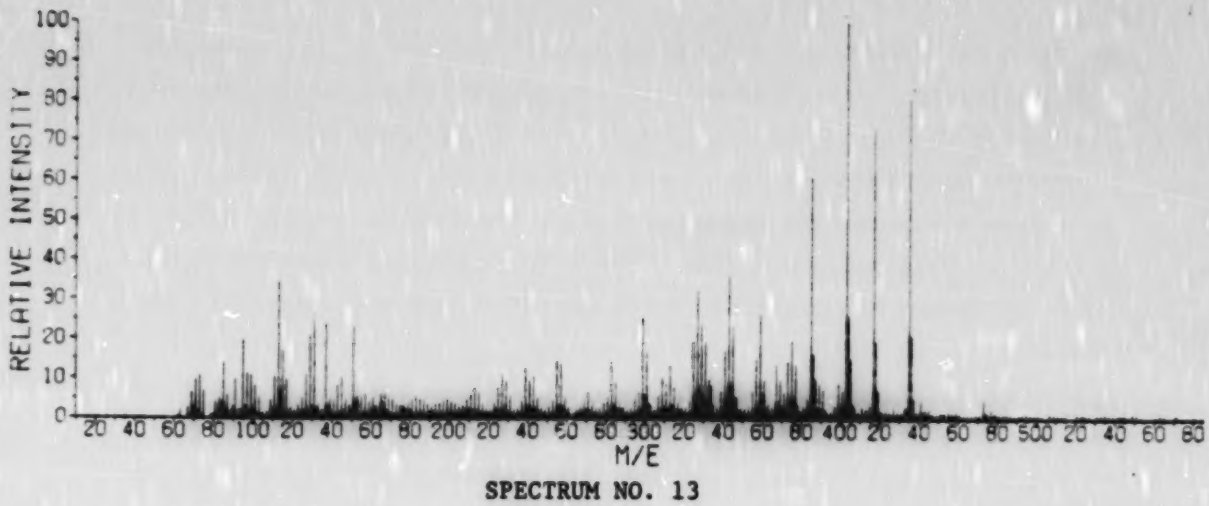


FIGURE 12. CHEMICAL IONIZATION MASS SPECTRUM OF 1-HEPTENE AEROSOL (SAMPLE M599). SUCCESSIVE SPECTRA RECORDED AS PROBE TEMPERATURE RAISED FROM 25 TO 200 C.

to one oxygen atom, a methylene unit, or to one oxygen atom less two hydrogen atoms. It is reasonable that components in the aerosol mixture would differ in this way, since photodegradation of organics under smog-chamber conditions involves oxidative removal of H-atoms, chain scission reactions, and incorporation of atmospheric oxygen.

The signals with the highest m/e appear in No. 10 with m/e 436. It is not known whether compounds of higher molecular weight were absent from the sample or simply were not sufficiently volatile to appear on our spectra. Another possible explanation for their absence is that such high-molecular weight species were not removed from the filter by our extraction procedure. To discount this alternative, we examined a filter sample containing 1-heptene aerosol in the mass spectrometer probe. Although signals with m/e up to several hundred were observed, the spectrum was very weak and could not be ascribed with certainty to aerosol alone.

To our knowledge, the presence of polymeric substances in hydrocarbon aerosols has not been demonstrated previously, although there has been some discussion in this regard.

Further work will be necessary to determine the nature of the cross-links in the polymers, which will provide a clue to the mechanism for formation of the aerosol.

E. Infrared Spectrum of 1-Heptene Aerosol.

The infrared spectrum of the methylene chloride extract of the aerosol from the 1-heptene/NO_x/SO_2 experiment was recorded as a film on sodium chloride plates. The spectrum is shown in Figure 13, and reveals strong absorption in the regions corresponding to frequencies where hydroxy, carbonyl groups, and C-O single bonds absorb. The only distinctive features are strong absorptions at 1620 and 1280 m^{-1} which correspond to strong bonds associated with organic nitrates (general structure $RONO_2$). Such compounds have been postulated to be present in urban atmospheric aerosols.[2] Although this result was interesting,

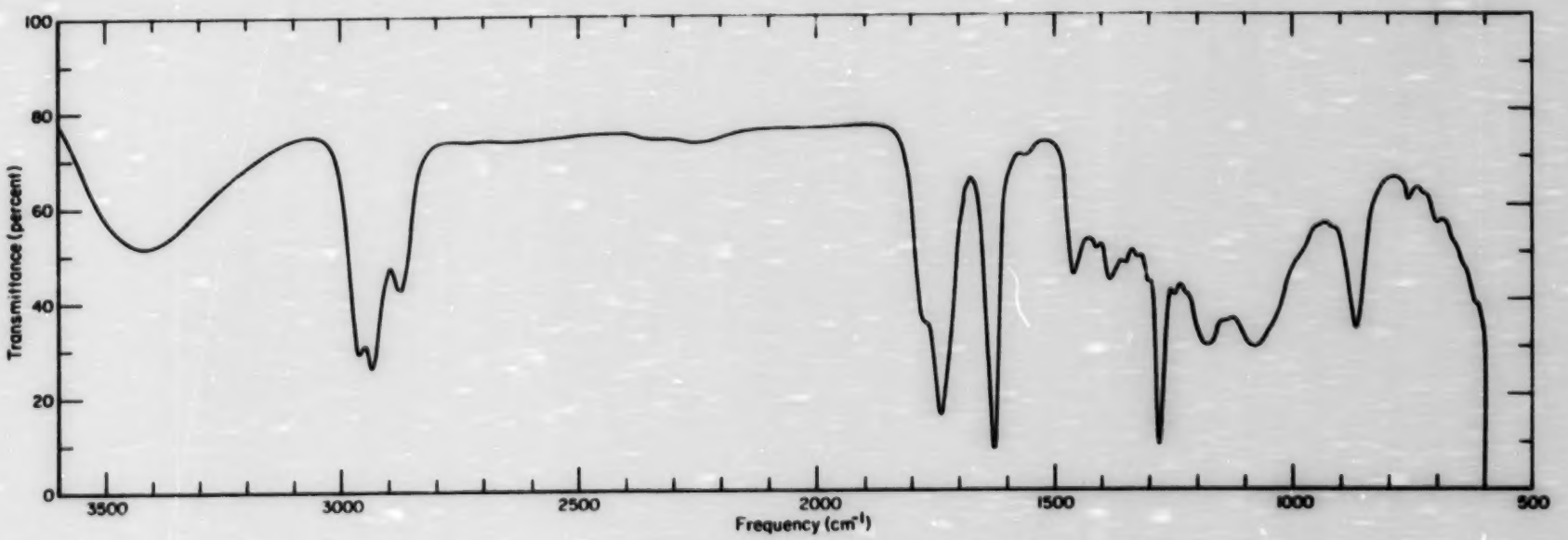


FIGURE 13. INFRARED SPECTRUM OF PRODUCTS IN METHYLENE CHLORIDE

we have not recorded other infrared spectra of our aerosols because the general features usually are not very informative. Similar spectra have been described in detail in an earlier report on model aerosols.

F. Analysis of Vapor Phase Organic Species Associated with Model Aerosols

Vapor phase species were collected using Chromosorb 102 chromatographic traps, following filtration by a pre-extracted quartz fiber filter. Approximately 300 liters of gas were sampled from the smog-chamber in each instance. The collected samples were recovered by thermal desorption, followed by freeze-out in a stainless steel sample loop; chromatographic injection was subsequently achieved through flash-heating the loop to 250 C and diverting the GC carrier gas through it, as described earlier. The three model aerosol systems chosen for this study were toluene/NO_x, toluene/NO_x/SO_2, and 1-heptene/NO_x/SO_2/NO_2. GC separation was achieved using a Silar SCP chromatographic column; GC-MS analysis was carried out by methane chemical ionization.

1. Analysis of Volatile Species Associated with Toluene Aerosol. Two experiments were carried out, one utilizing toluene/NO_x/SO_2, and the other in the absence of SO_2. The objectives were to determine what volatile products were formed, and how these differed from the species associated with filterable particulate, and also to determine whether sulfur-containing species were associated with the more volatile aerosol products.

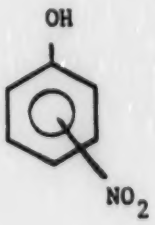
Striking differences from the previous analysis of the particulate aerosol material were immediately evident in both experiments. The products observed had undergone little or no oxidative degradation, and a considerable degree of ring substitution had taken place. Relatively minor differences were observed between the two experiments, and no organic sulfur-containing compounds were detected. All major products were common to both experiments, except one, and eight of the nine major products contained a nitro group.

As might be expected on the basis of free radical oxidation, benzaldehyde, phenol, and three isomers of nitrotoluene have been

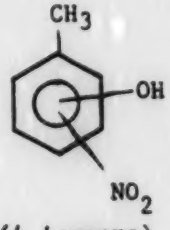
tentatively identified on the basis of their methane ionization mass spectra. Additionally, one isomer of nitrophenol has been tentatively identified in each reaction system. We are presently unable to assign a structure to three further products which are common to each experiment, these compounds most probably have molecular weights of 122, 112, and 90. One major peak which appears to be a polar compound and to have a molecular weight of 122 was found only in the toluene/$NO_x SO_2$ system, although this material does not appear to contain sulfur. The mass spectrum of this latter compound is consistent with methyl-p-benzoquinone, which will be identified conclusively when an authentic sample is received for comparison.

While four isomeric nitrocresols were found in both of these systems, only two were previously found in filterable particulate from a similar toluene/NO_x system.[3] However, the vapor sampling/analysis system permits significantly higher sensitivity which could account for this apparent discrepancy, since two of the isomers were of relatively minor concentration. Surprisingly, nitrotoluene was not previously observed in filtered aerosol particulate, yet all three possible isomers were observed in this study. We are unable to explain the presence of styrene and ethyl styrene, other than to attribute them to contamination or impurities in the original toluene.

In summary, the following species have been determined on both toluene/NO_x and toluene/$NO_x SO_2$ systems. No sulfur organics were detected.



(3 isomers)



(4 isomers)

The reconstructed gas chromatograms for the respective GC-MS analysis are shown in Figures 14 and 15; tentatively identified compounds are indicated on the figures, and the mass spectra for peaks in the toluene/NO_x/SO_2 experiment are included in Appendix B.

2. Analysis of Volatile Species Associated with 1-Heptene Aerosol. Gas chromatographic analysis of the organic vapors associated with 1-heptene/NO_x/SO_2 aerosol provides a remarkably simple well resolved chromatogram. Unfortuantely, the subsequent GC-MS analysis of this sample by methane ionization has presented some difficulty. The six major products give high quality spectra, but since they are all presumably aliphatic, the spectra leave open a very wide range of possibilities with regard to interpretation. The spectral assignments indicated on Figure 16 must at this stage be regarded as speculative, although they are not inconsistent with the mass spectra of the major peaks which are presented in Appendix C.

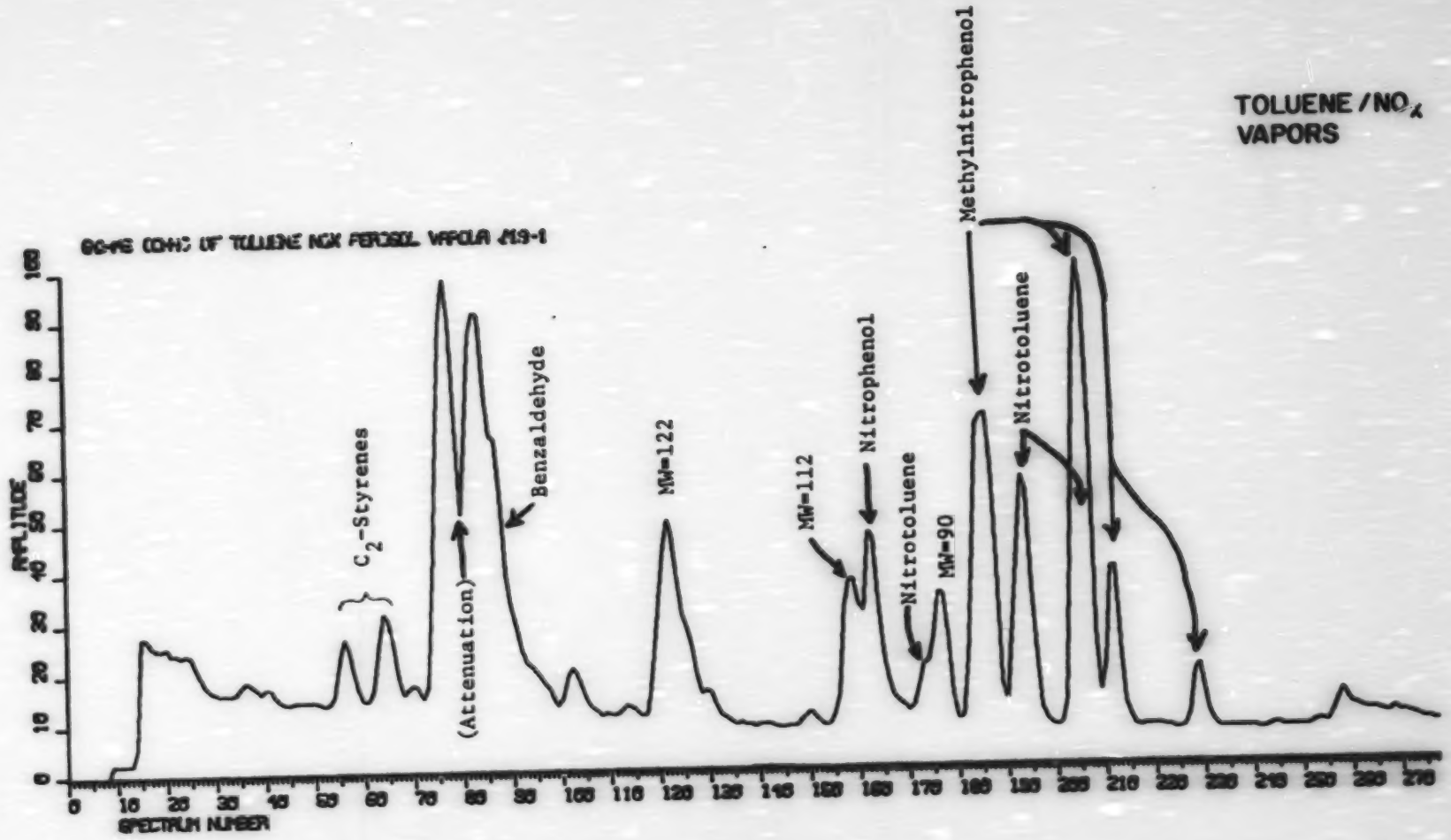


FIGURE 14. METHANE IONIZATION GC-MS ANALYSIS OF VAPOR PHASE ORGANIC COMPOUNDS ASSOCIATED WITH TOLUENE/NO_x AEROSOL

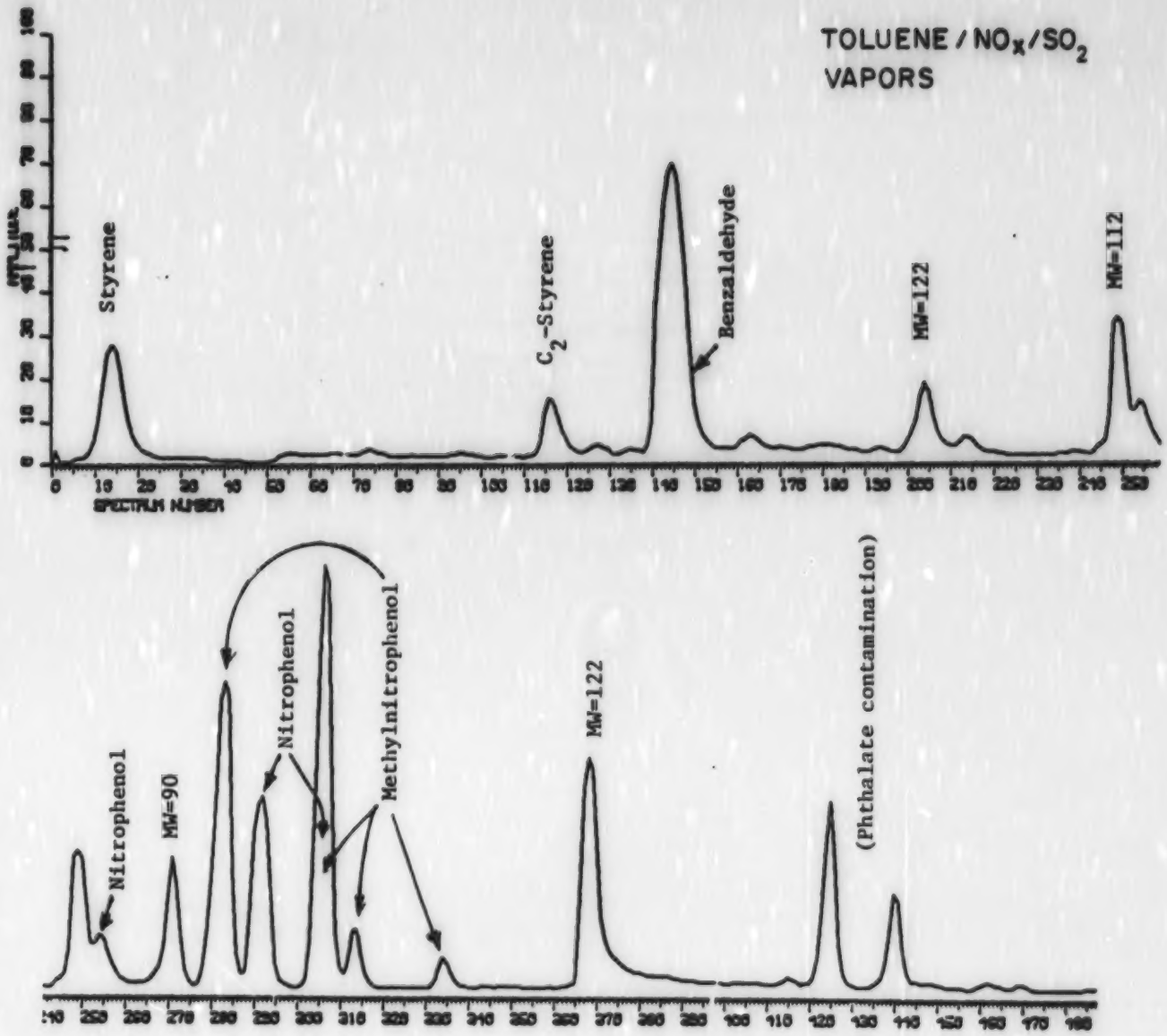


FIGURE 15 METHANE IONIZATION GC-MS ANALYSIS OF VAPOR PHASE ORGANIC COMPOUNDS ASSOCIATED WITH TOLUENE/NO_x/SO_2 AEROSOL

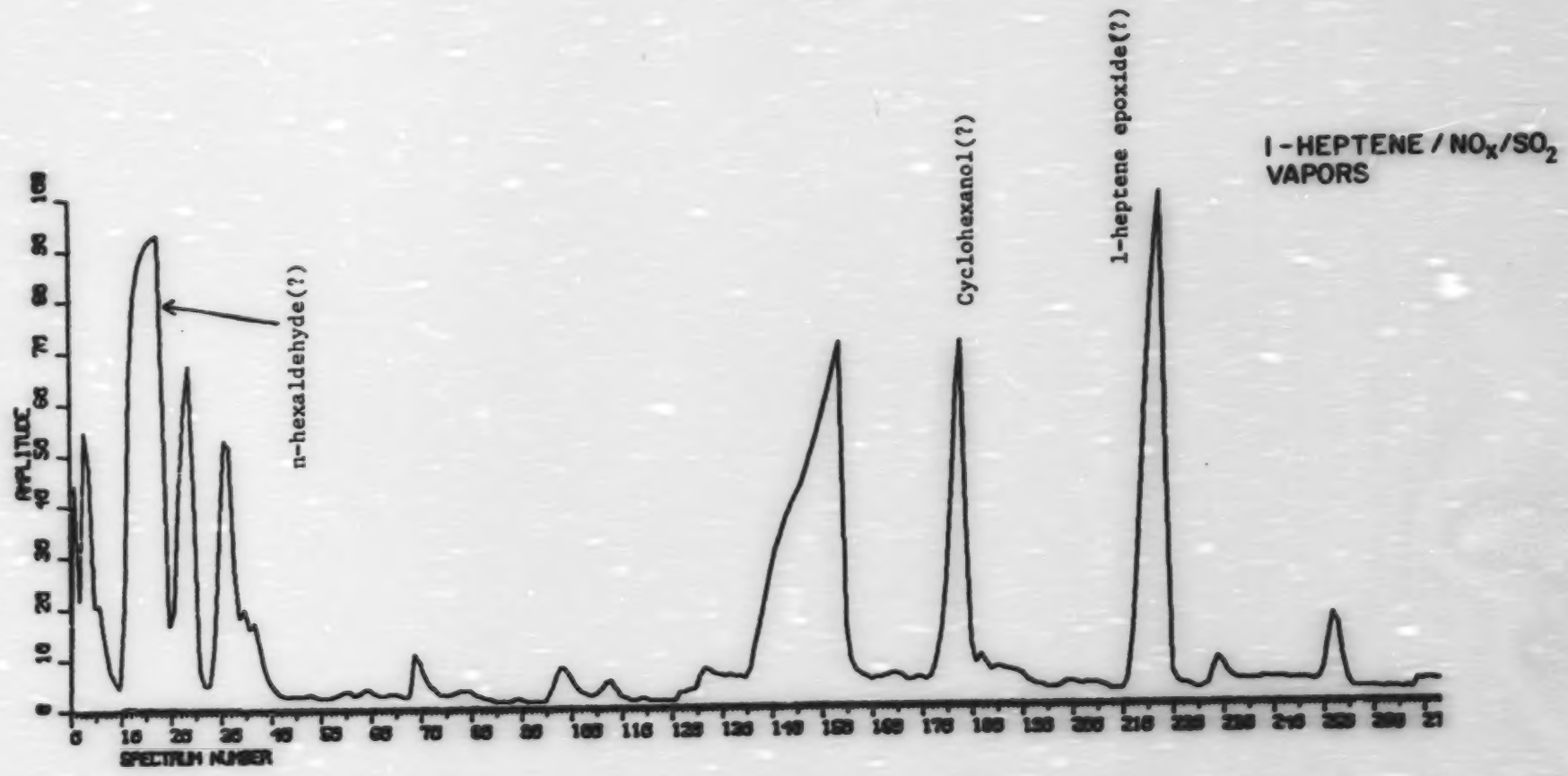
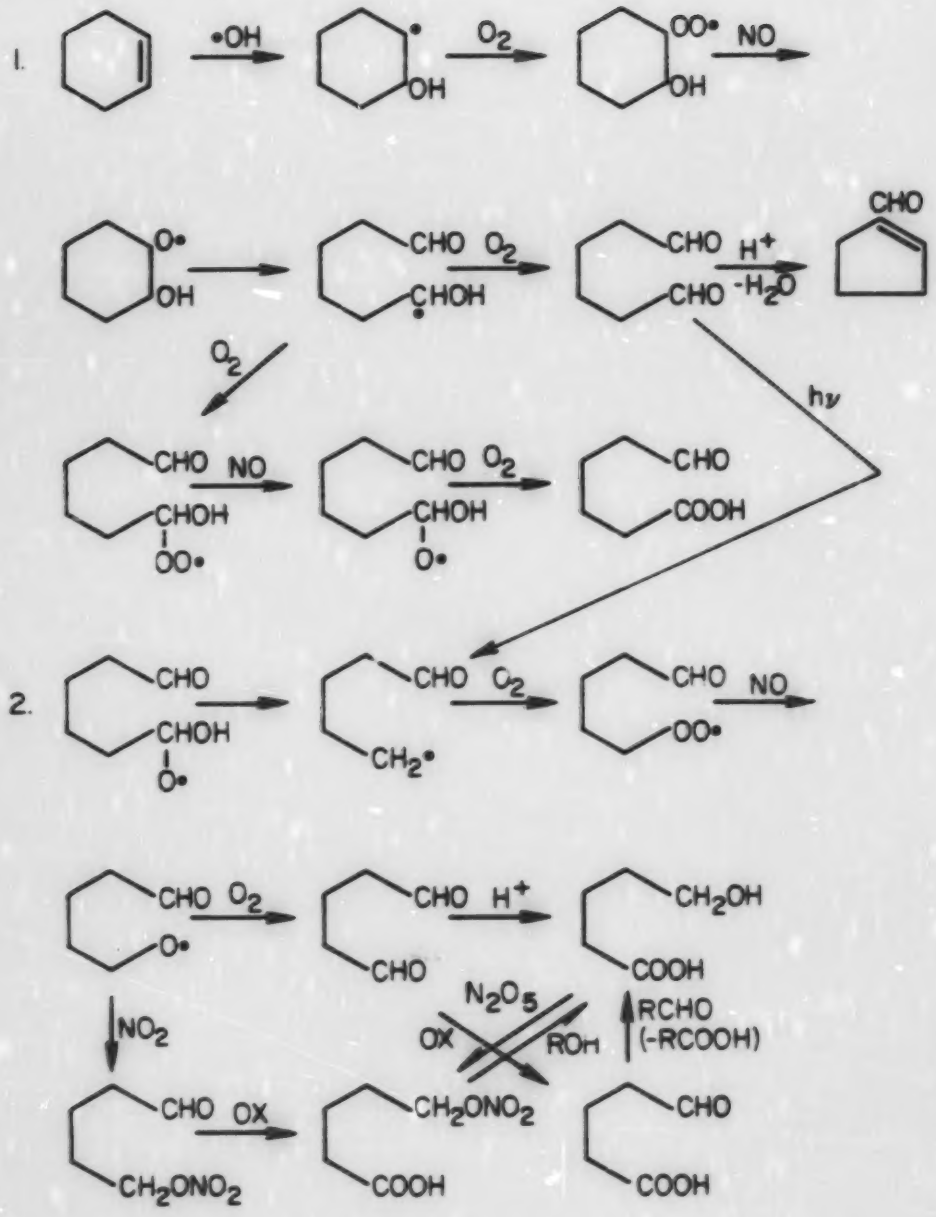


FIGURE 16. METHANE IONIZATION GC-MS ANALYSIS OF VAPOR PHASE ORGANIC COMPOUNDS ASSOCIATED WITH 1-HEPTENE/NO_x/SO_2 AEROSOL

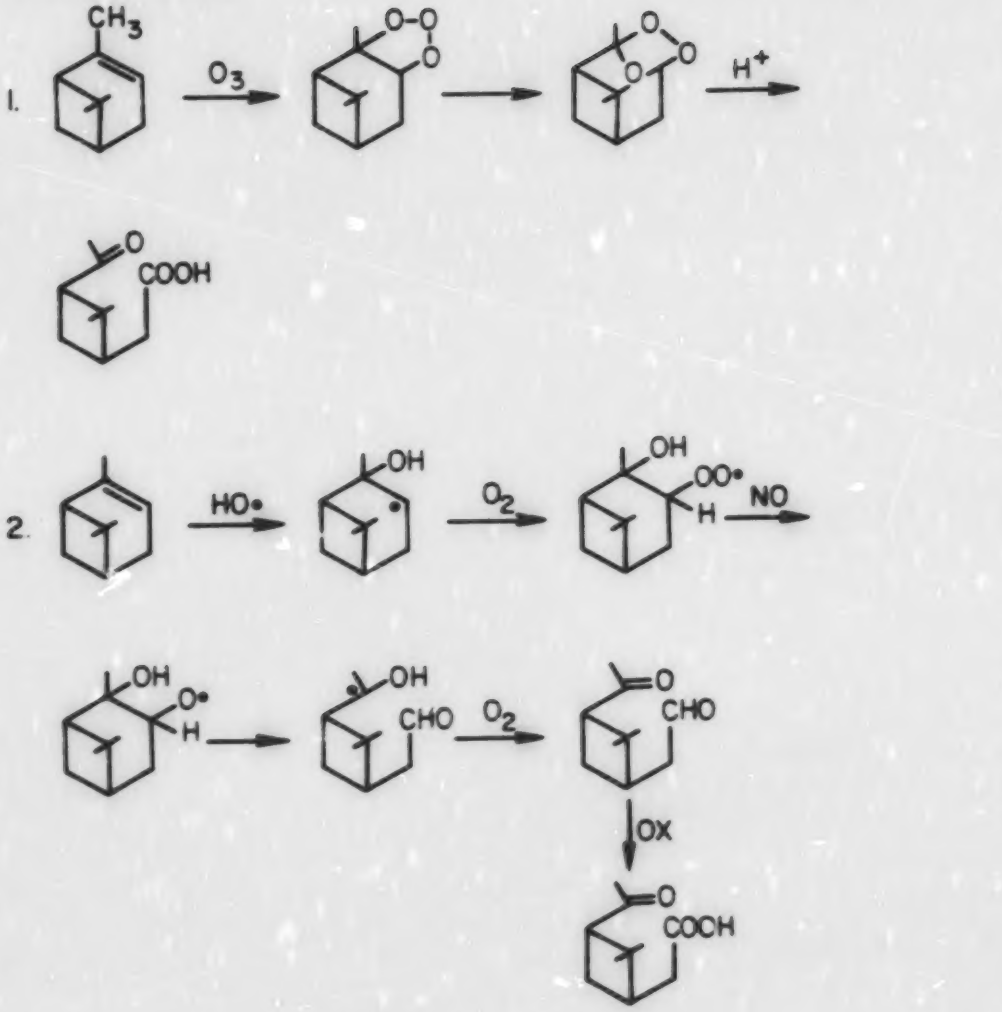
G. Reaction Types and Mechanisms Infrared from Tentatively Identified Reaction Products in Model Aerosols

On the basis of reactions which are known to occur during smog formation, it is possible to write reasonable mechanisms leading to the products that we have tentatively identified from different aerosol precursors (see Background section). Some mechanisms we favor are as follows.

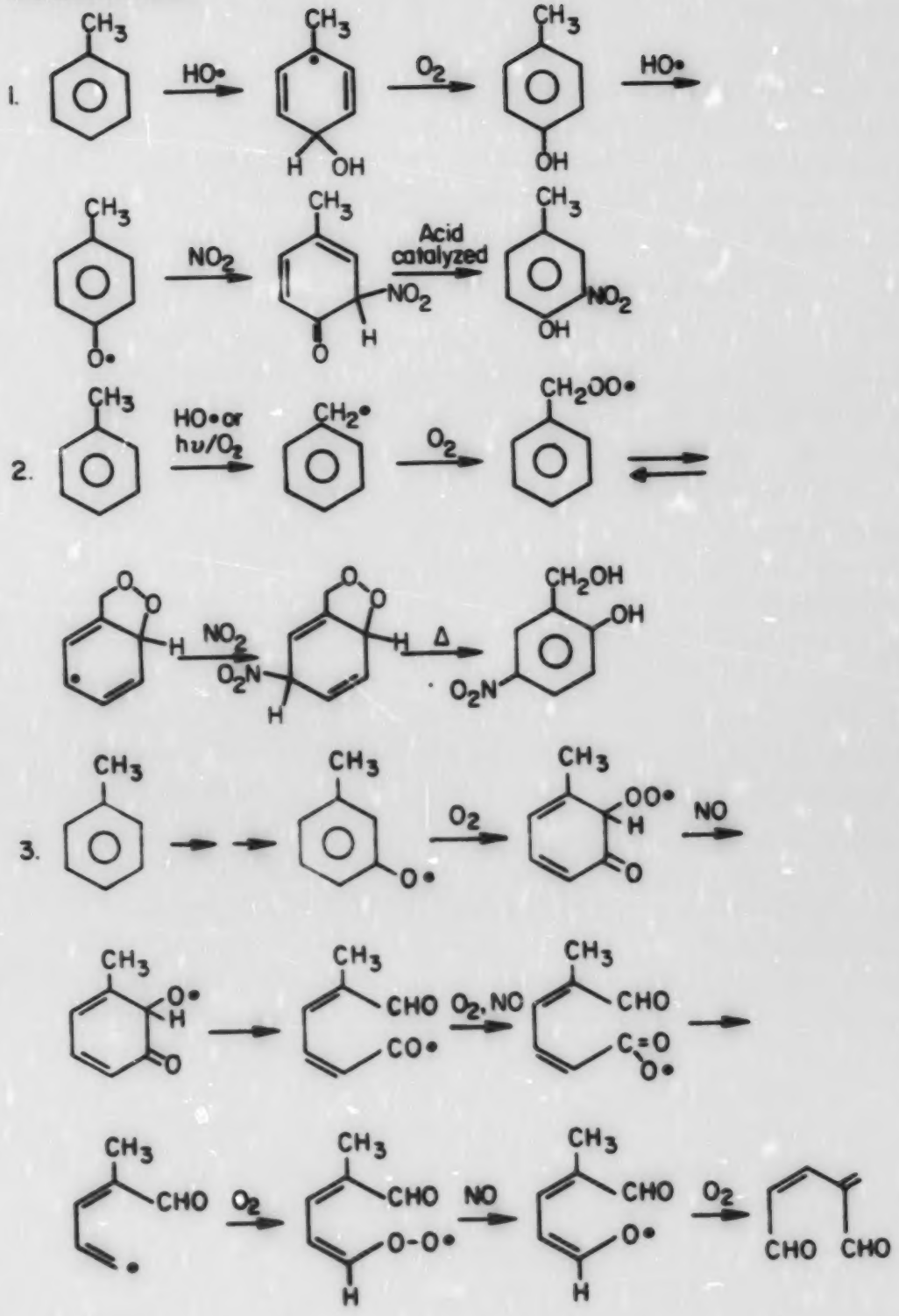
Cyclohexene products



α - Pinene products



Toluene products



The above reactions are rather obvious ones, and we have not tried to include every plausible route to each compound. The most interesting feature in the products, from a mechanistic point of view, are the large number of terminal alcohol groups. These represent a relatively reduced functionality, and it is difficult to write many homogeneous gas-phase mechanisms from the starting materials we studied, which give alcohols as products. We have accordingly considered many redox reactions in our mechanisms involving aldehyde disproportionations:

$$RCHO + R'CHO \rightarrow RCH_2OH + R'COOH.$$

This type of reaction is given as "ox" in the mechanisms, and presumably would take place within the aerosol droplets. If the reducing aldehyde is formaldehyde, the product is formic acid. Both of the latter compounds are known constituents of atmospheric smog.

The ring-operated products from toluene can be explained in a simple fashion if we invoke β-scission in alkoxy radicals, which we postulate as intermediate species. Nitration and hydroxylation of toluene probably occur by a free-radical mechanism as depicted above, followed by rearrangements of the radical adducts that probably take place in the condensed phase. On the other hand, cresols (hydroxytoluenes) are quite reactive toward nitration in solution, and it is therefore also reasonable that the nitrocresols may be formed from nitric acid and cresols within the aerosol drops or at surfaces, rather than as shown above.

It should be emphasized that neither the mechanisms nor the nature of the products are firmly established. Many products can be generated on paper by slight variations of the above reaction paths, that are not observed (or have not been identified) by our analytical procedures. Future work will render the nature of the reactions more certain.

H. Health Effects

The toxic doses and safety limits for concentrations of the compounds tentatively identified in the vapor and particulate phases in this work are given in Table 4. The compounds that appear in brackets

TABLE 4. TOXICOLOGY OF COMPONENTS IN TOLUENE AND 1-HEPTENE-DERIVED AEROSOLS

Compound	Toxicology
4-Nitro-m-cresol	ipr-mus LDLo:500 mg/kg
2-Nitro-p-cresol	orl-rat LD50:3360 mg/kg
m-,o-, and p-Nitrotoluene	USOS-air: TWA 5 ppm (skin)
[Nitroglycerin	USOS 2 mg/m^3 (0.22 ppm) (skin)]
[p-Benzoquinone	USOS air: TWA 0.1 ppm]
2-Methyl-p-benzoquinone	orl-rat LDLo 250 mg/kg
Benzaldehyde	orl-rat LD50: 1300 mg/kg
n-Hexaldehyde	ihl-rat LCLo: 2000 ppm/4H
[1,2-Epoxybutane	ihl-rat LCLo: 4000 ppm]

Source: NIOSH Toxic Substances List, 1974

are related to ones tentatively identified, since data on few of the more oxidized toluene products are available. (Nitroglycerin has been included because two strong bands in the IR spectrum of the crude 1-heptene aerosol supported the presence of organic nitrates.)

In polluted atmospheres, the concentration of particulate is usually below 100 $\mu g/m^3$, of which about one quarter is organic. If an average molecular weight of 200 in the organic portion is assumed, the upper limit of organic pollutant concentration in the aerosol is about 0.01 ppm. The toxic levels and safety thresholds in Table 4 are all considerably above this value. Although (1) much of the data in Table 4 pertains to animal studies, (2) many of the figures refer to doses administered by means other than inhalation, and (3) amounts less than the lethal doses cited may cause tissue damage, it does not appear that any of the organic compounds tentatively identified poses an immediate health hazard. On the other hand, we cannot discount long-term effects on humans of inhalation of such compounds in small quantities, either alone or in combination with other pollutants.

In particular, many of the compounds identified in our study are present in, or related to components of embalming preparations (Table 5). The function of the aldehydes in such preparations is to coagulate and harden protein, while the alcoholic constituents lower the surface tension of the liquid and promote diffusion of the aldehydes into tissue.[4] A different cellular phenomenon for which aldehydes (in particular, malondialdehyde) are held responsible, is the appearance of fluorescent pigments (age pigments) in living tissues in amounts that increase with the age of the organism. Such pigments are thought merely to accompany oxidative reactions of lipids,[5] although their formation involves cross-linking reactions that may cause loss in tissue resiliency. Compounds containing multiple aldehyde groups, which may react in the same manner to induce cross-linking, were identified tentatively in earlier work in these laboratories[6] and elsewhere.[2]

TABLE 5. COMPONENTS OF EMBALMING FLUID PREPARATIONS

Formaldehyde	Phenol
Glutaraldehyde	Glycerin
Benzaldehyde	Salicylic Acid
Furfural	tert-Butanol
Water	Methanol
	Hydroxymethylcellulose

Sources: Bennet, "The Chemical Formulary"; Kirk-Othmer, "Encyclopedia of Chemical Technology"

I. Conclusions

Although product identifications for many of the oxidized species are tentative, the overall picture of the fate of toluene and 1-heptene under simulated urban atmospheric conditions is what we would reasonably expect. The initial oxidation processes give relatively simple, identifiable derivatives that are found on gas phase sampling. The particulate aerosol products from both hydrocarbons are more highly oxidized, and hence more polar and less volatile. For 1-heptene the aerosol consists in part of compounds of high molecular weight that are formed by condensation of species arising from different heptene molecules. The fact that conventional derivatization fails to render either aerosol more than about 30% volatile is consistent with the presence of several functional groups in the molecules or with a high molecular weight. Sulfur dioxide and sulfuric acid aerosol do not give appreciable quantities of new compounds detectable by our approach when included in the toluene runs.

All of the products identified from the vapor or aerosol phase in toluene and 1-heptene are present in concentrations that do not appear to present a direct health hazard in the quantities expected in urban atmospheres. The composition of the model aerosols and oxidized species in the vapor, however, resembles that of several embalming fluids that owe their preservative action in part to reactions of aldehyde components with tissue protein. The effects on humans of organic aerosols over extended periods, either alone or in synergism with other pollutants, therefore, may be significant.

REFERENCES

(1) Jones, P.W., Report No. 74-265, 67th APCA Meeting, Denver, Colorado, (June 9-13, 1974).

(2) Schuetzle, D., Cronn, D., Crittenden, A. L., and Charlson, R. J., Environ. Sci. Tech., 9, 838 (1975).

(3) Miller, D. F., Schwartz, W. E., Gemma, J. L., and Levy, A. "Haze Formation - Its Nature and Origin", Battelle Columbus Laboratories, Final Report to the U.S. Environmental Protection Agency (Contract No. 68-02-0792) and the Coordination Research Council (March, 1975).

(4) Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd ed., Interscience, 19, Col. 8, p. 100.

(5) See e.g., Chio, K. S., and Tappel, A. L. Biochemistry, 8, 2821 (1969).

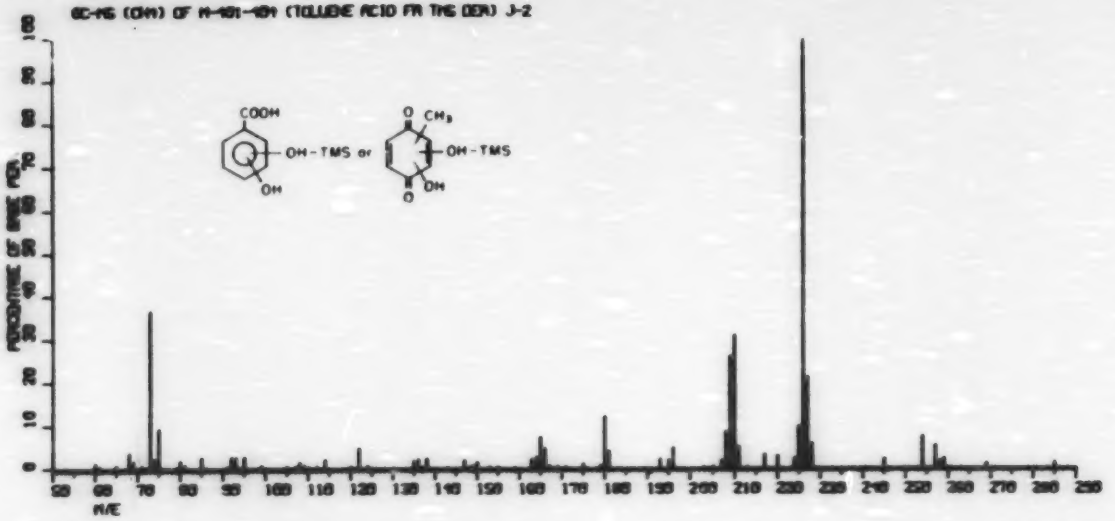
(6) Schwartz, W. E., "Chemical Characterization of Model Aerosols", Battelle-Columbus Laboratories, Final Report to the U.S. Environmental Protection Agency, Grant No. 801174, (August, 1974).

APPENDIX A

METHANE IONIZATION SPECTRA OF COMPOUNDS OBSERVED ON THE GC-MS ANALYSIS (FIGURE 10) OF TOLUENE AEROSOL, DERIVATIZED WITH BSTFA

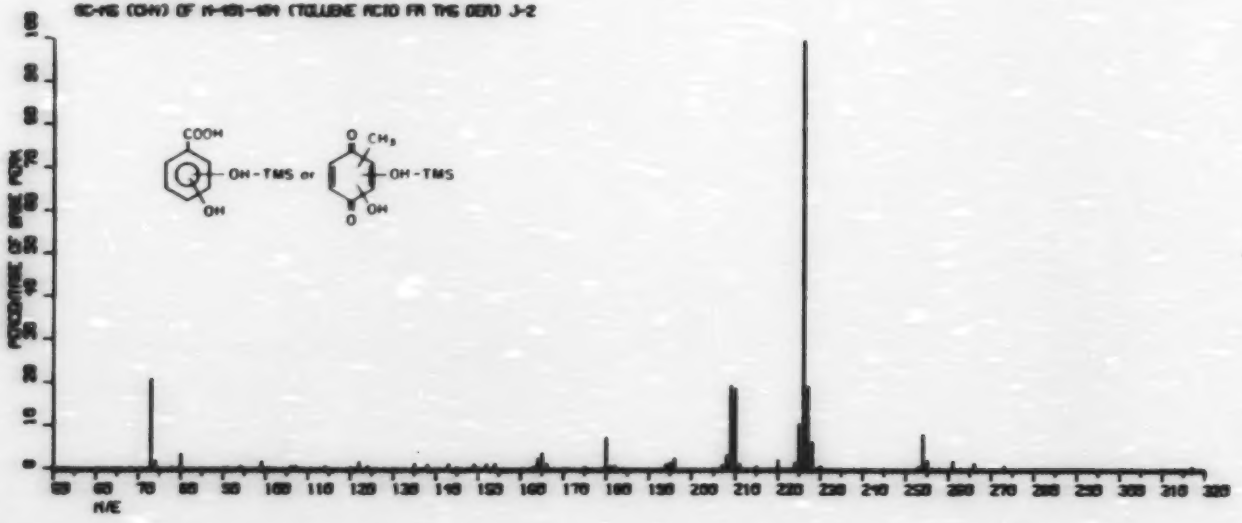
SPECTRUM 209 - 201

GC-MS (CHN) OF M-401-404 (TOLUENE ACID FR THS DER) J-2



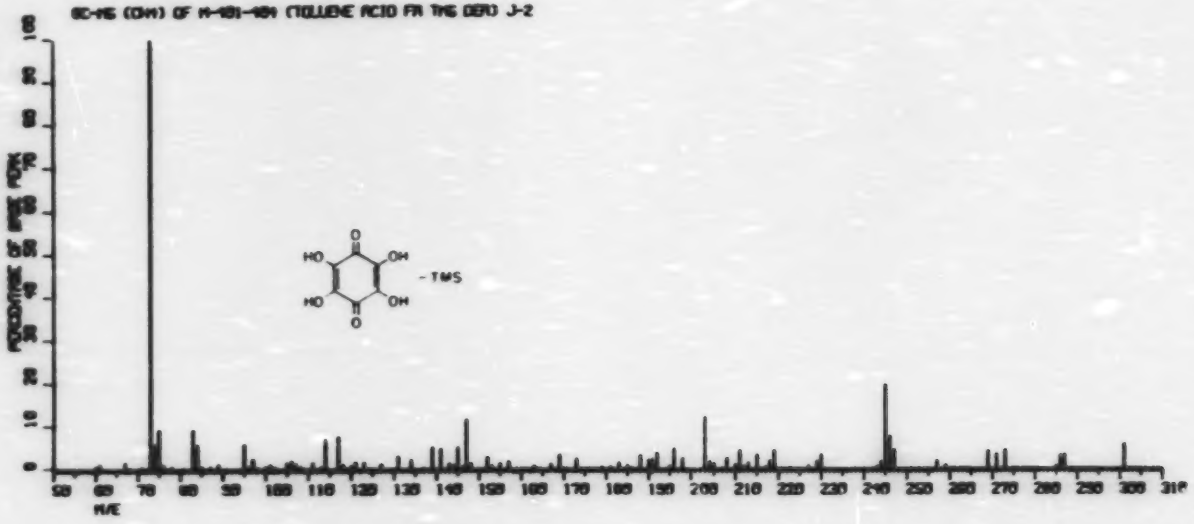
SPECTRUM 212 - 209

GC-MS (CHN) OF M-401-404 (TOLUENE ACID FR THS DER) J-2



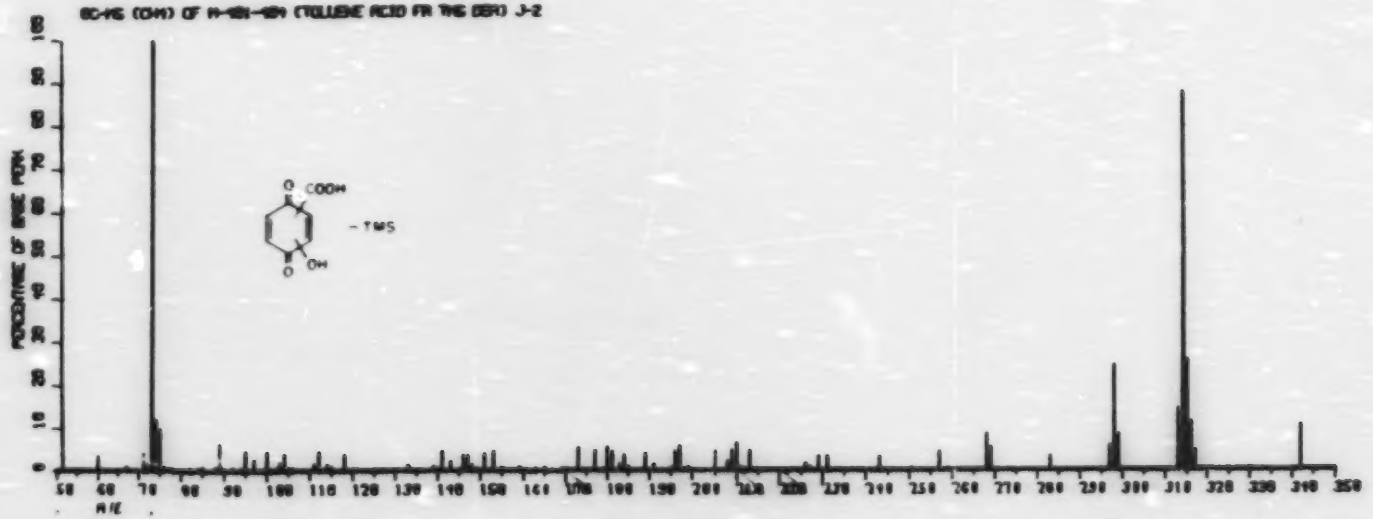
SPECTRUM 224 - 223

GC-MS (CHI) OF M-401-404 (TOLUENE ACID FR THG DER) J-2



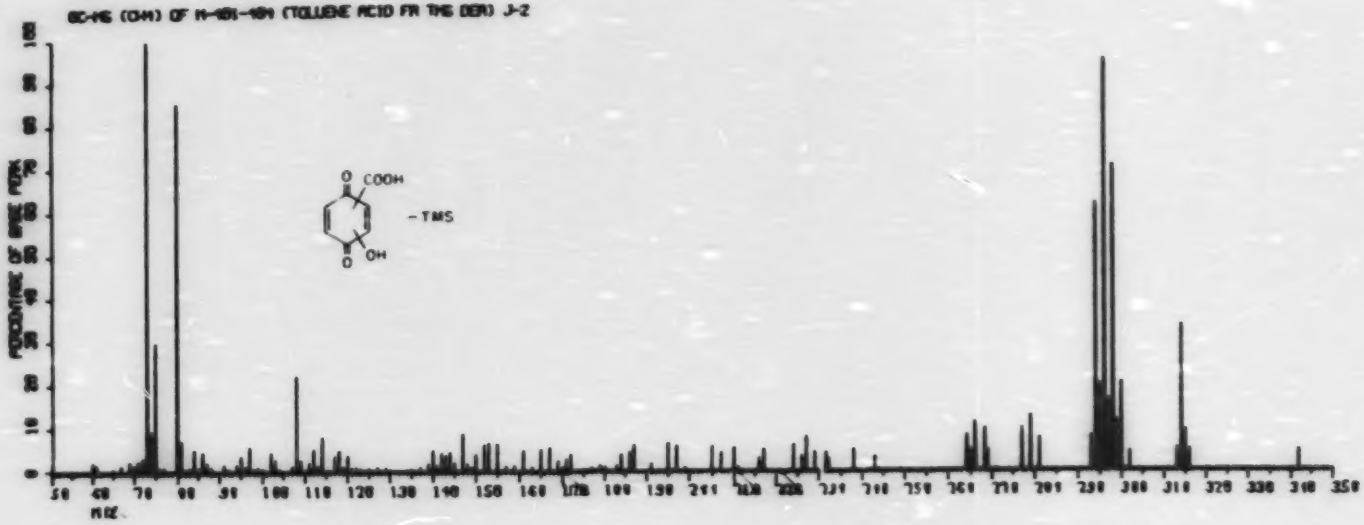
SPECTRUM 253 - 250

GC-MS (CHI) OF M-401-404 (TOLUENE ACID FR THG DER) J-2



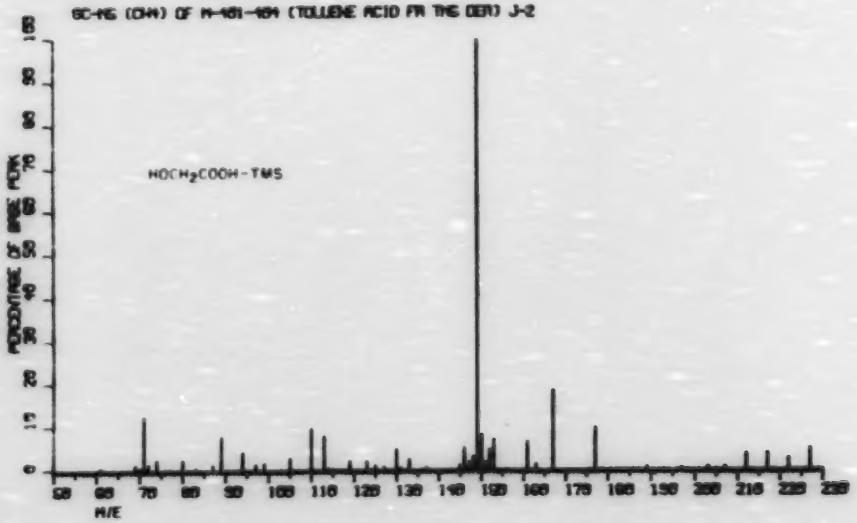
SPECTRUM 262-259

GC-MS (CHH) OF M-481-484 (TOLUENE ACID FR THS DER) J-2



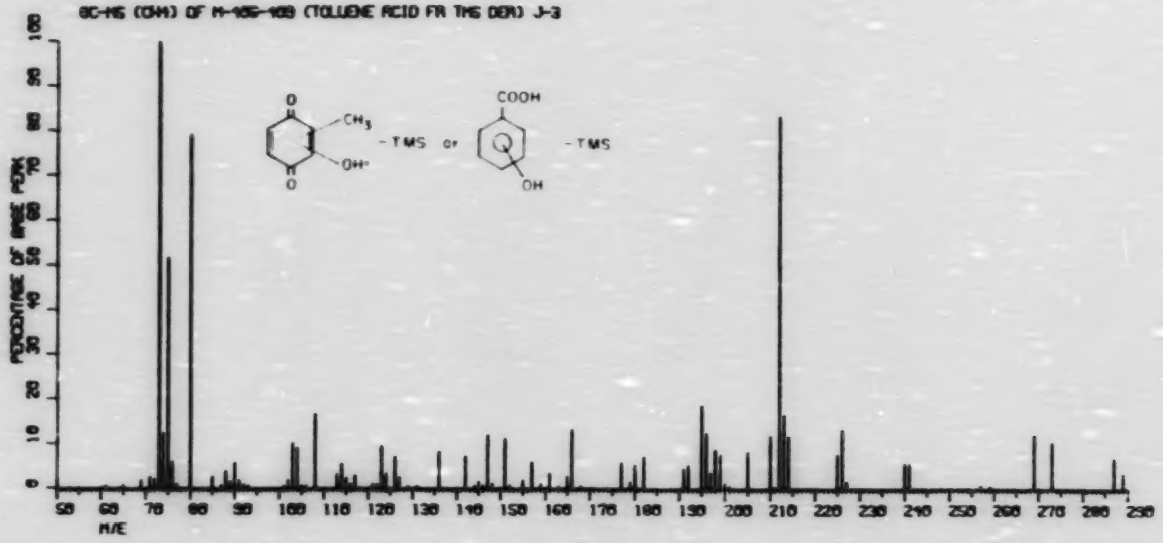
SPECTRUM 372 - 370

GC-MS (CHH) OF M-481-484 (TOLUENE ACID FR THS DER) J-2



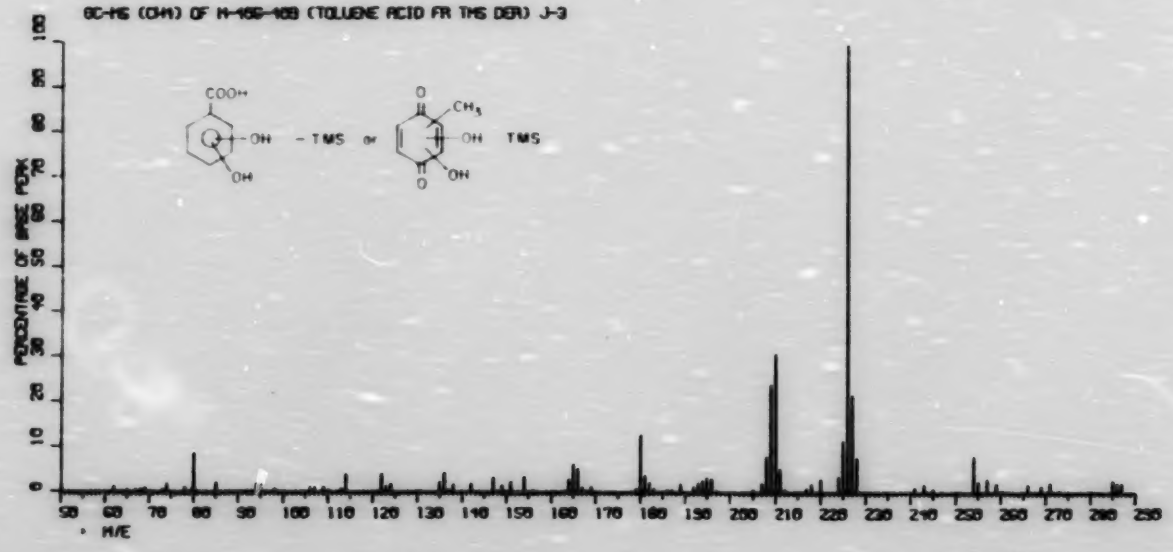
SPECTRUM 173 - 171

GC-MS (CHH) OF M-465-469 (TOLUENE ACID FR TMS DER) J-3



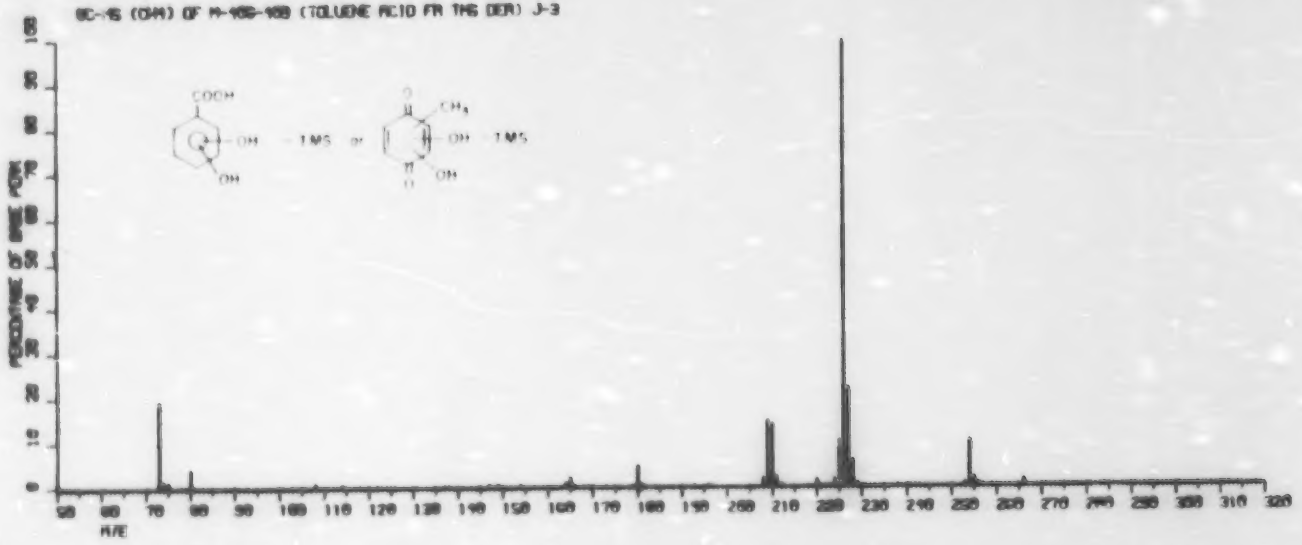
SPECTRUM 163 - 181

GC-MS (CHH) OF M-465-469 (TOLUENE ACID FR TMS DER) J-3



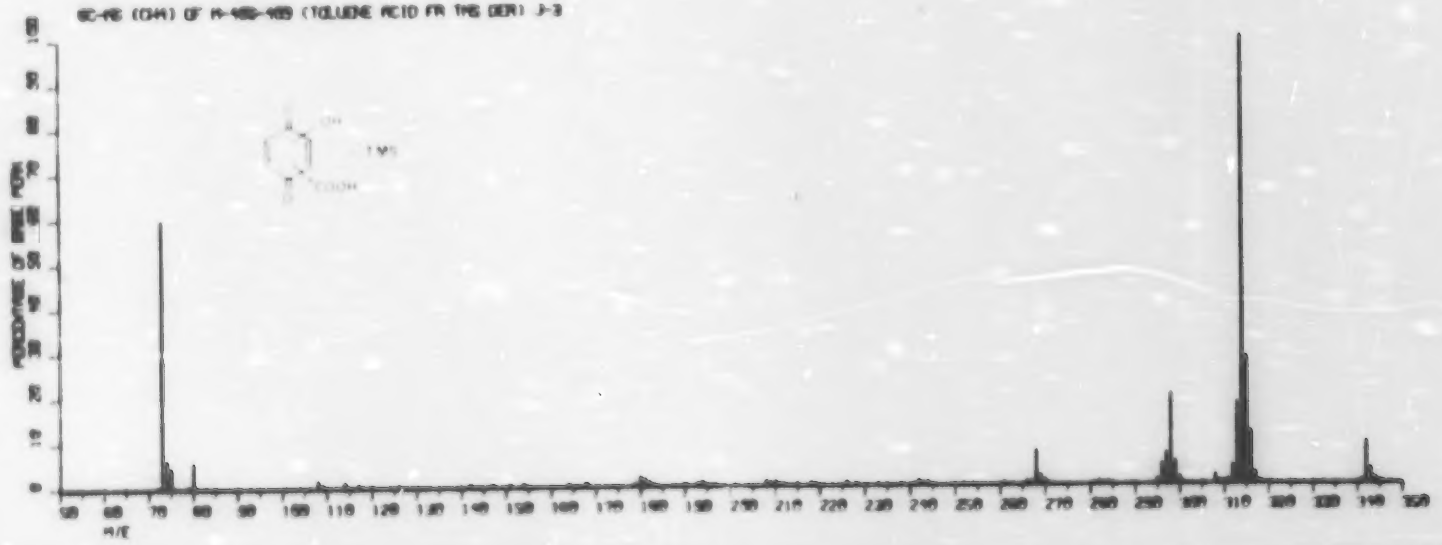
SPECTRUM 188 - 185

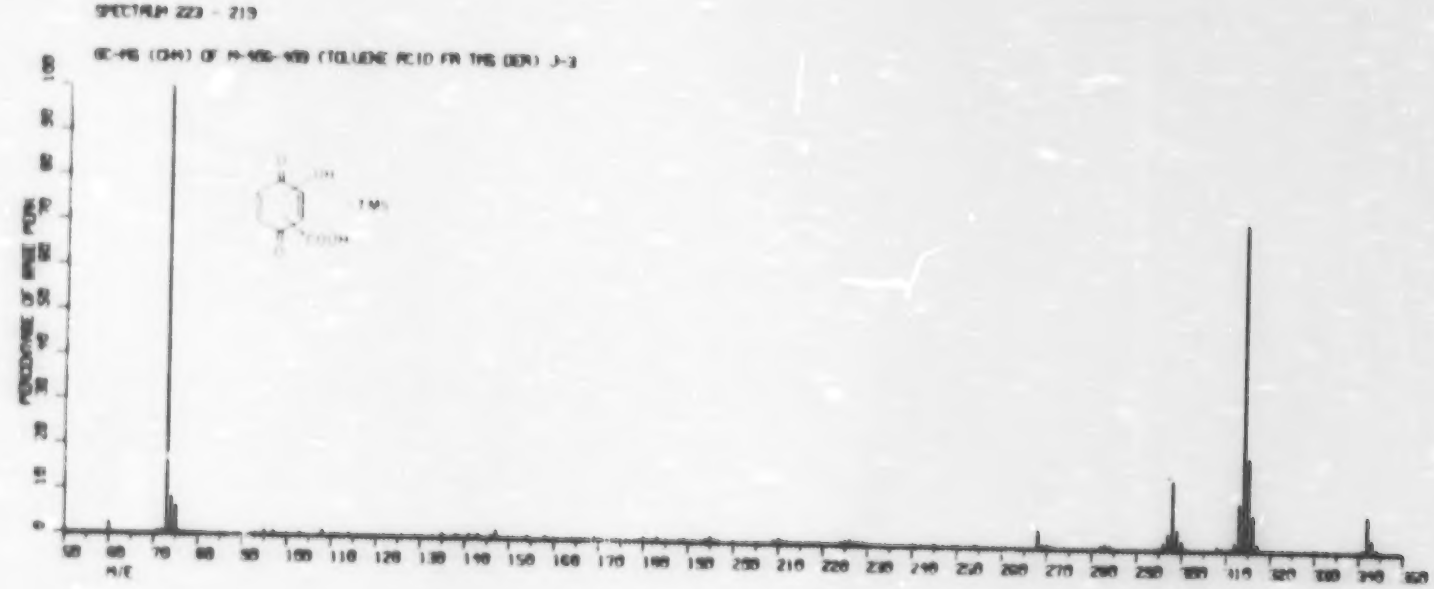
BC-45 (OH) OF M-488-488 (TOLUENE ACID FR THS DER) J-3

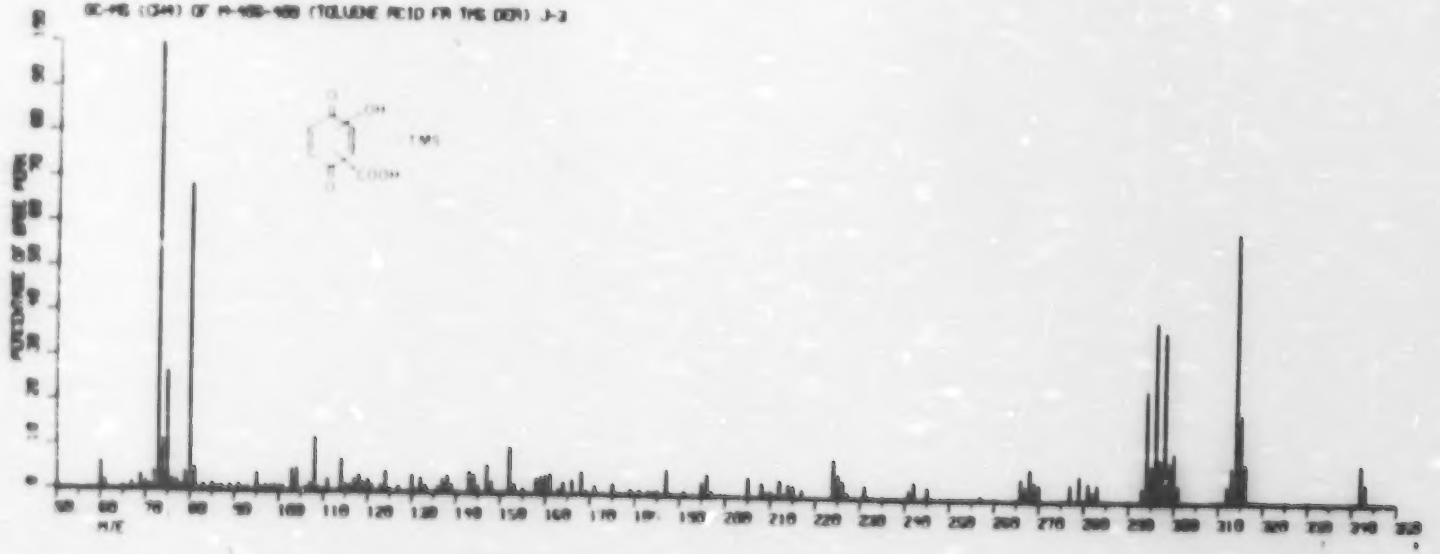


SPECTRUM 214 - 212

BC-46 (OH) OF M-488-488 (TOLUENE ACID FR THS DER) J-3





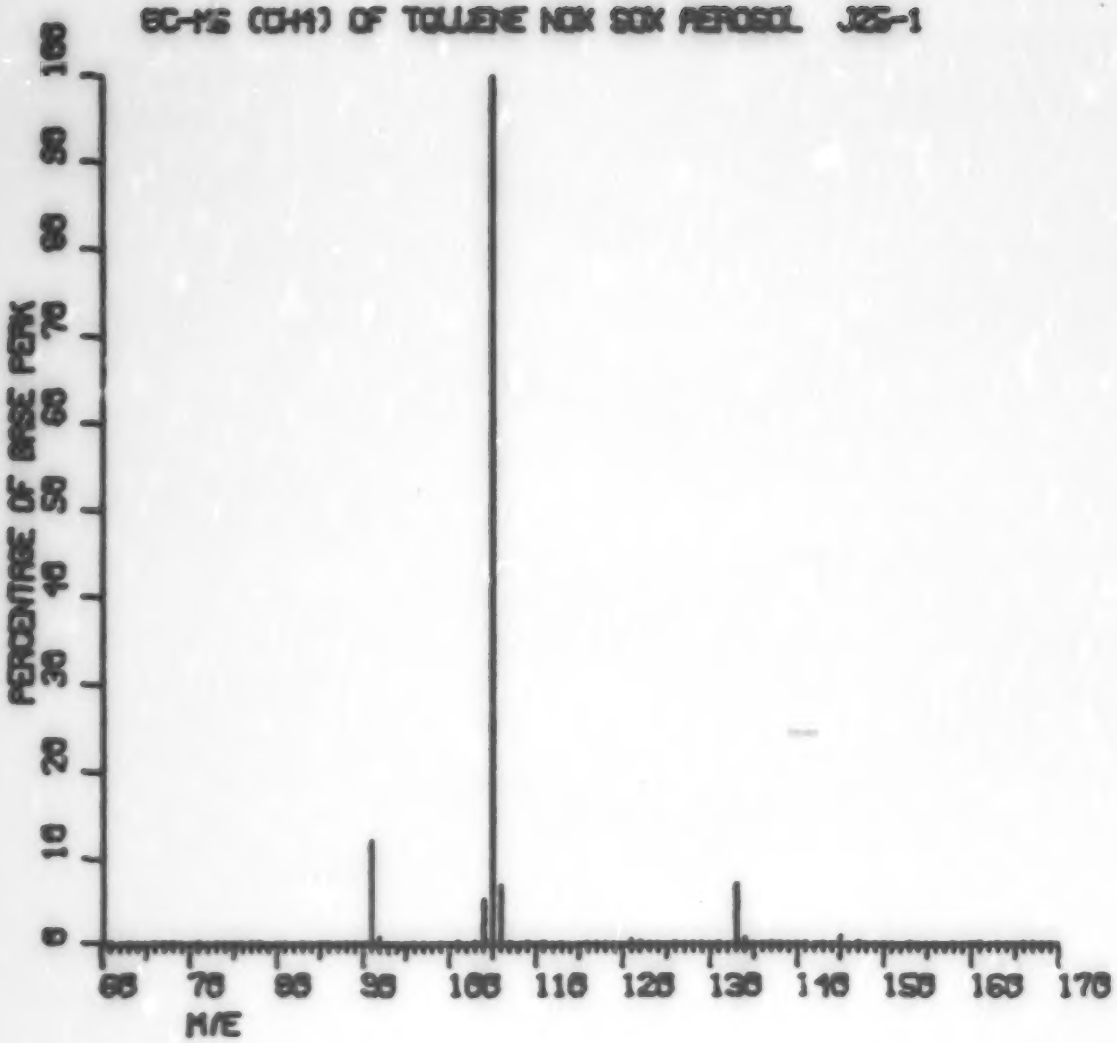


APPENDIX B

METHANE IONIZATION SPECTRA OF COMPOUNDS TENTATIVELY IDENTIFIED ON THE GC-MS ANALYSIS (FIGURE 15) OF VAPORS ASSOCIATED WITH TOLUENE/NO_x/SO_2 AEROSOLS

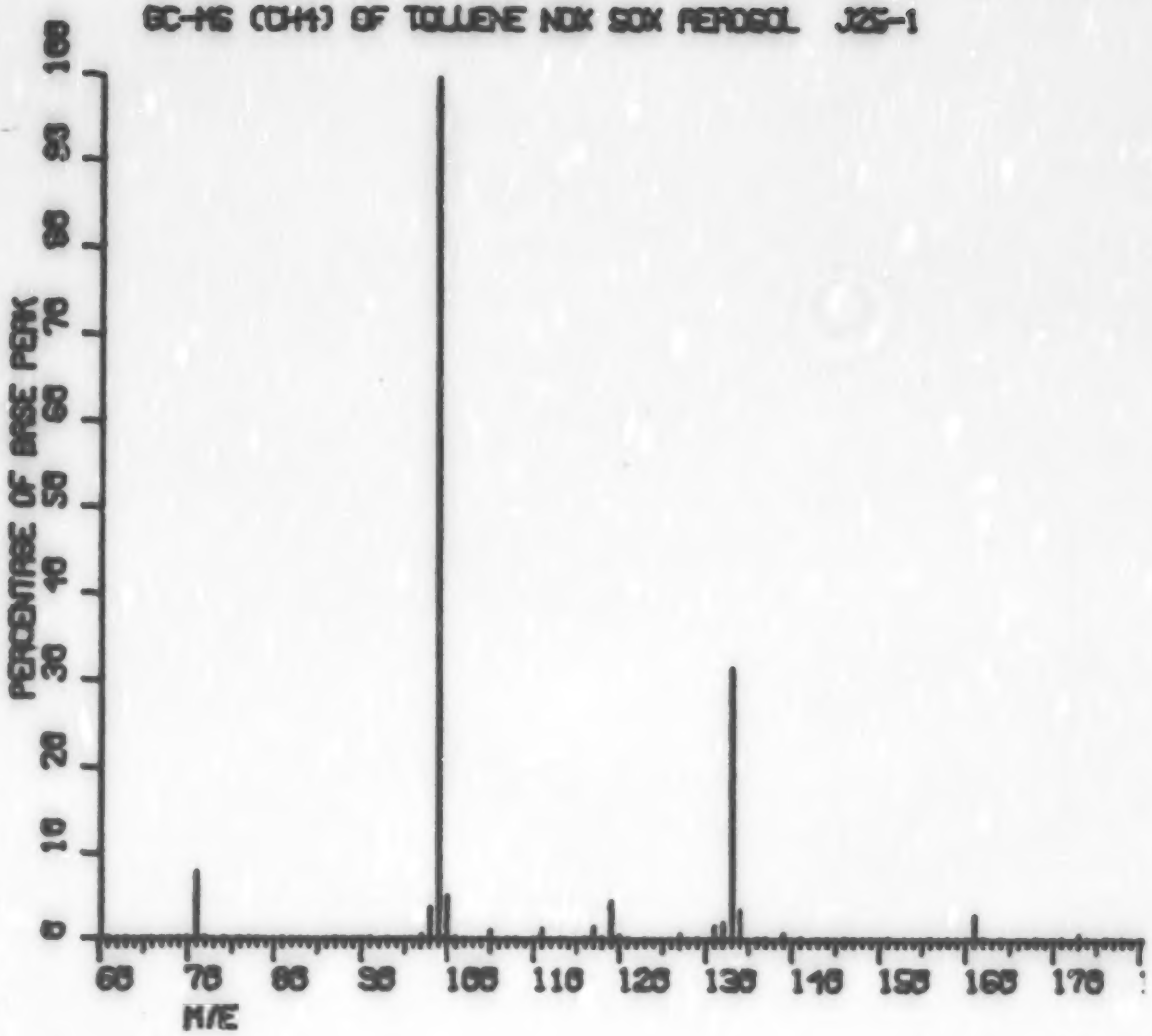
SPECTRUM 14 - 8

EC-HS (CH4) OF TOLUENE NOX SOX AEROSOL J2S-1



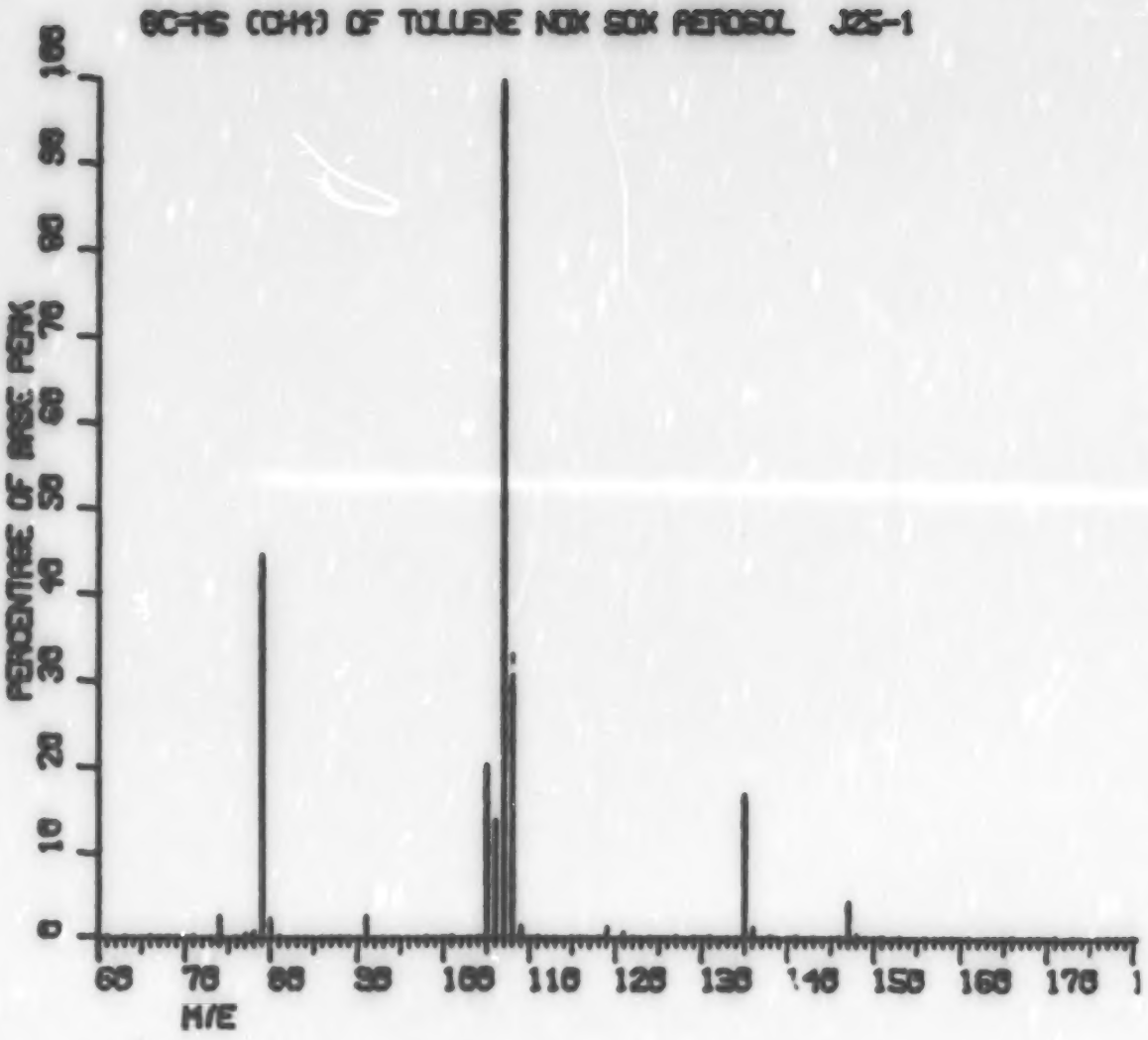
SPECTRUM 116 - 112

GC-MS (CH4) OF TOLUENE NOX SOX AEROSOL J25-1



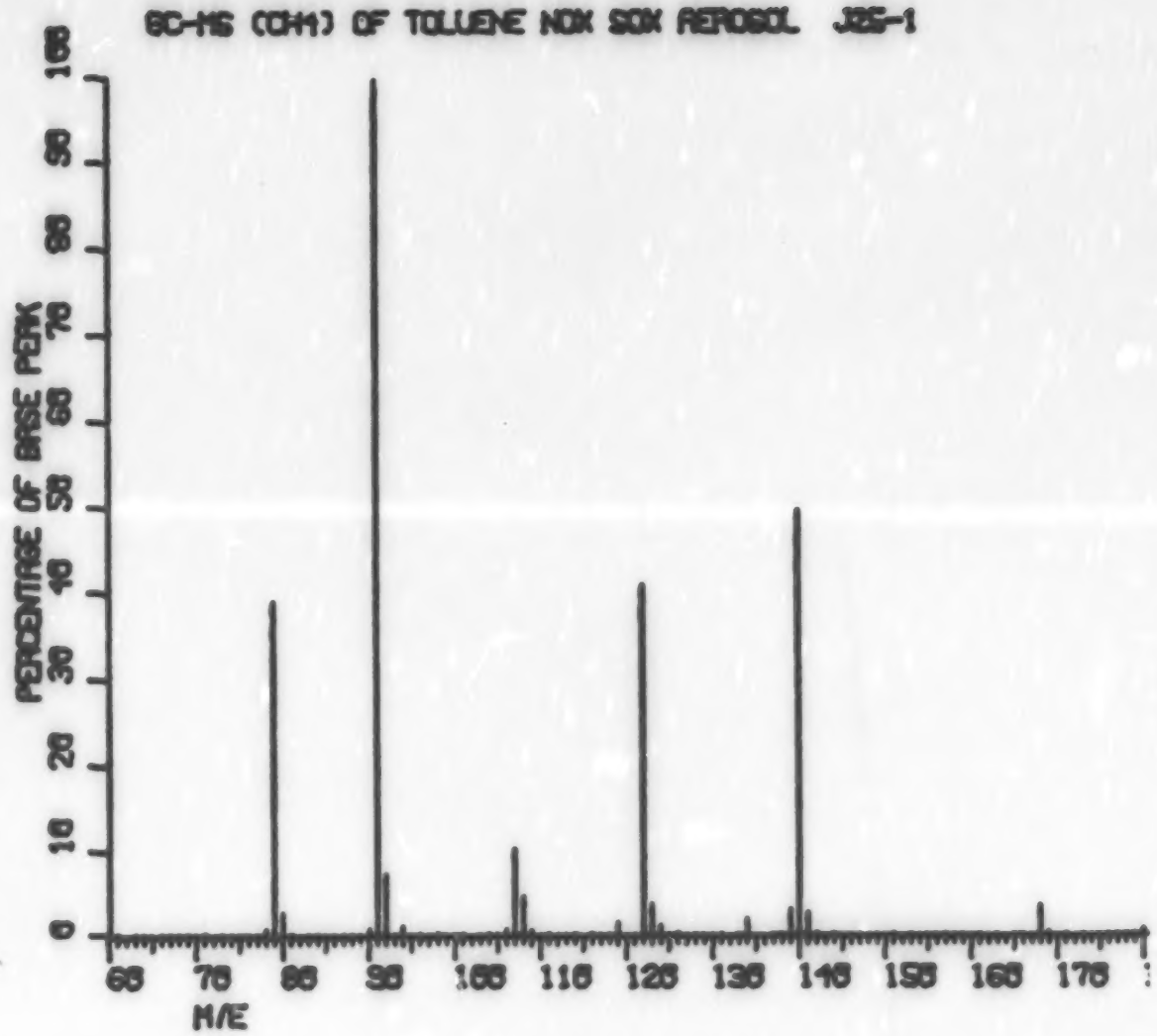
SPECTRUM 145 - 137

BC-HS (CH4) OF TOLUENE NOX SOX AEROSOL J25-1



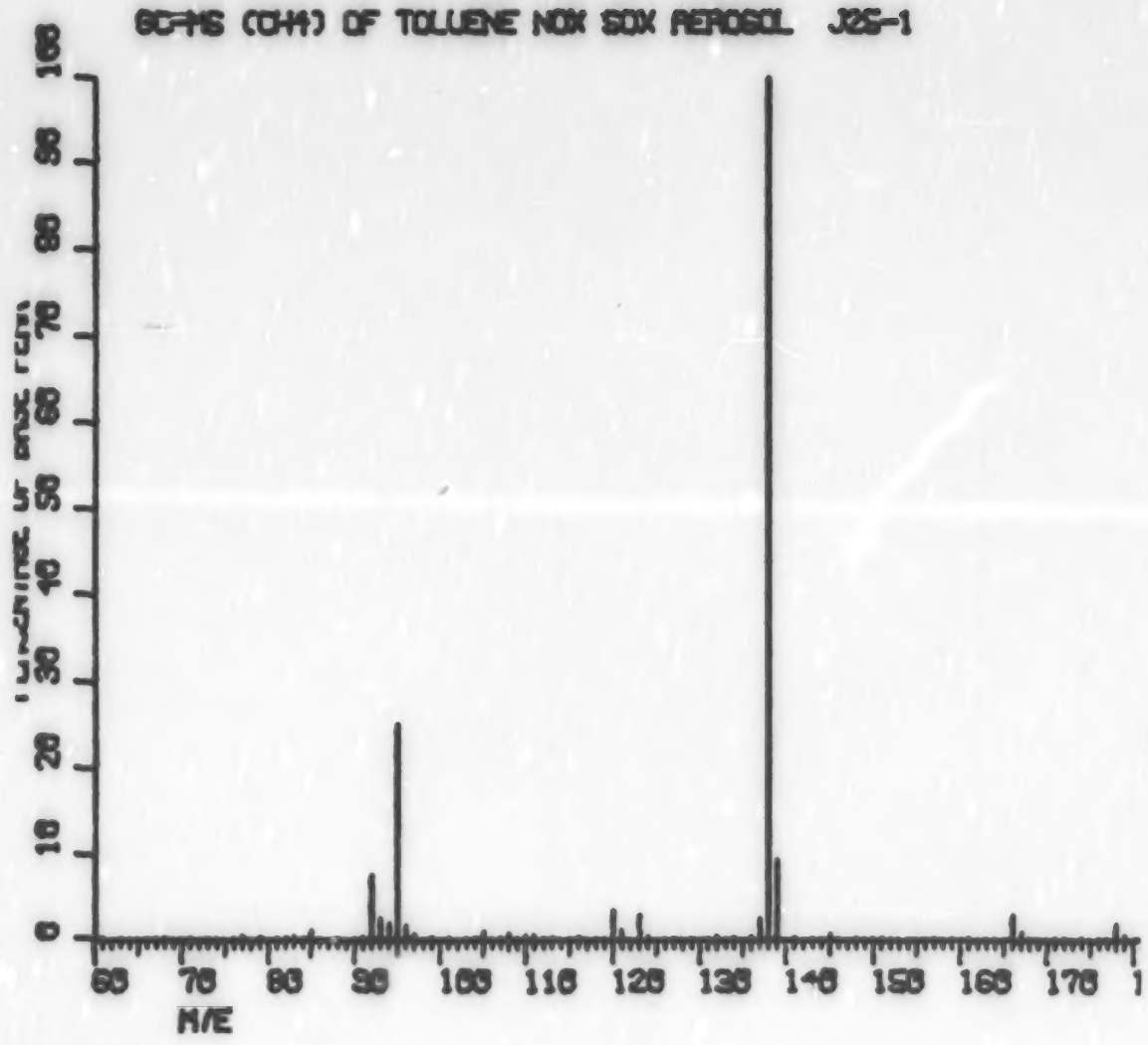
SPECTRUM 254 - 252

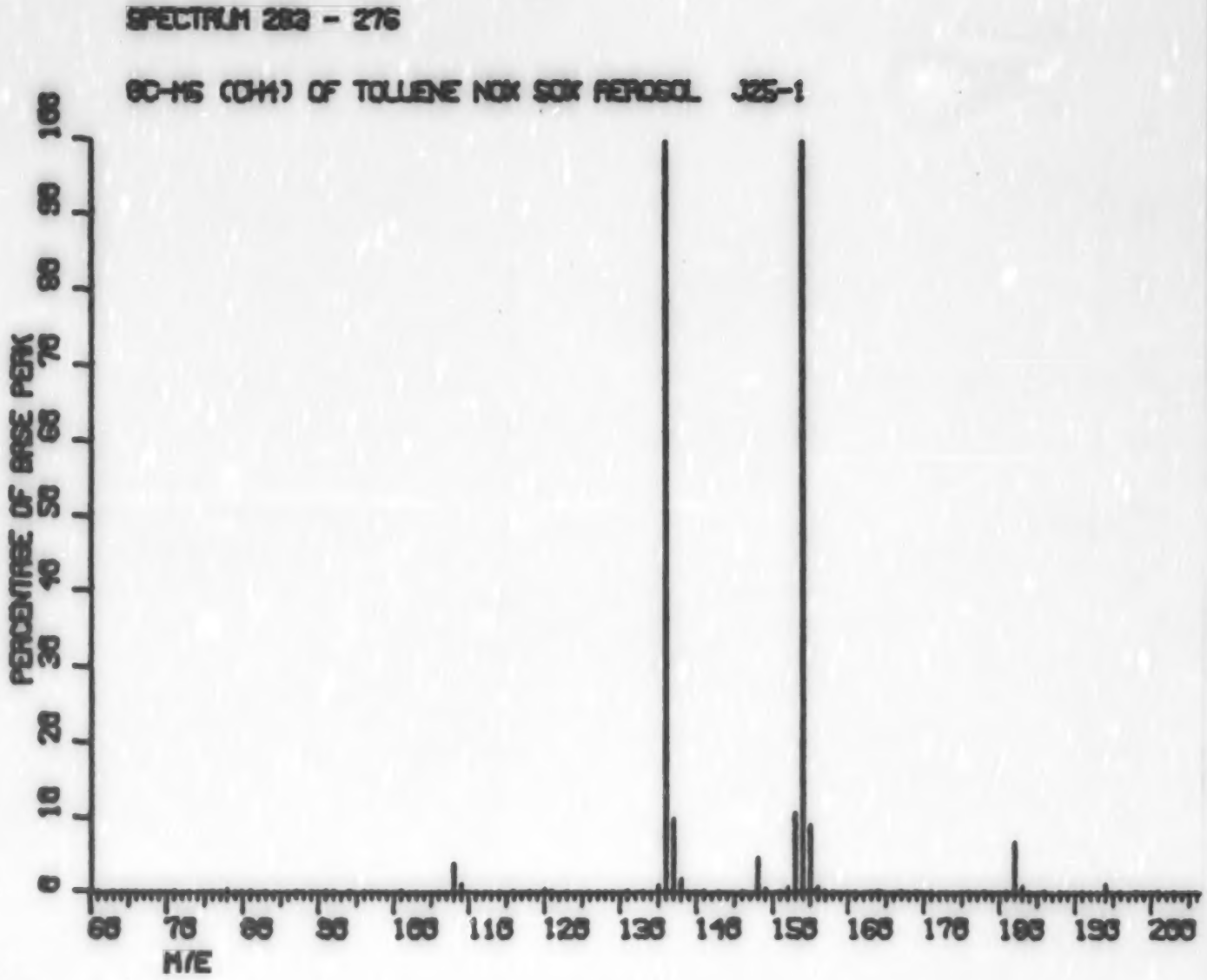
BC-HS (OH-) OF TOLUENE NOX SOX AEROSOL J25-1



SPECTRUM 267 - 264

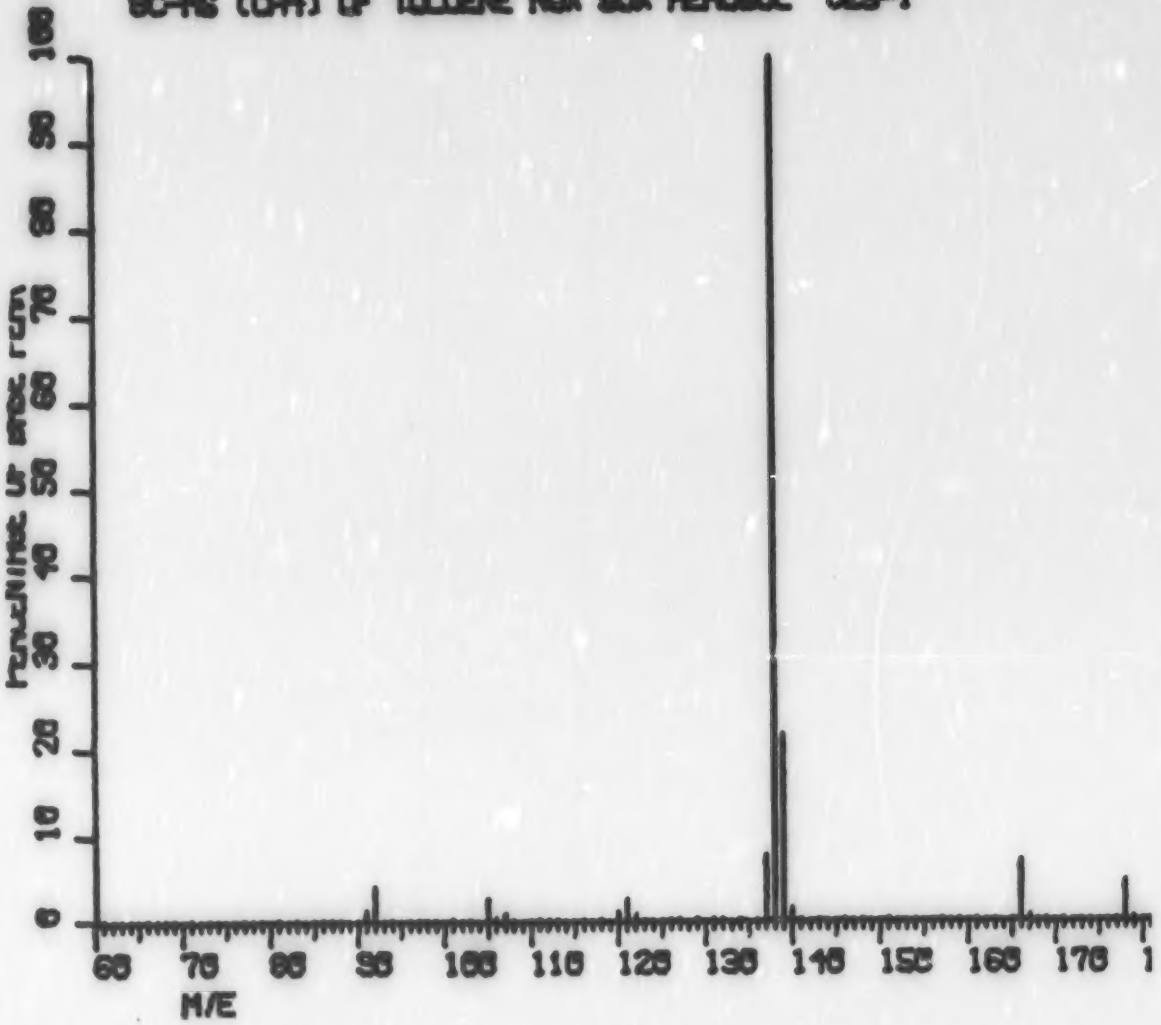
GC-MS (CH4) OF TOLUENE NOX SOX AEROSOL J2S-1

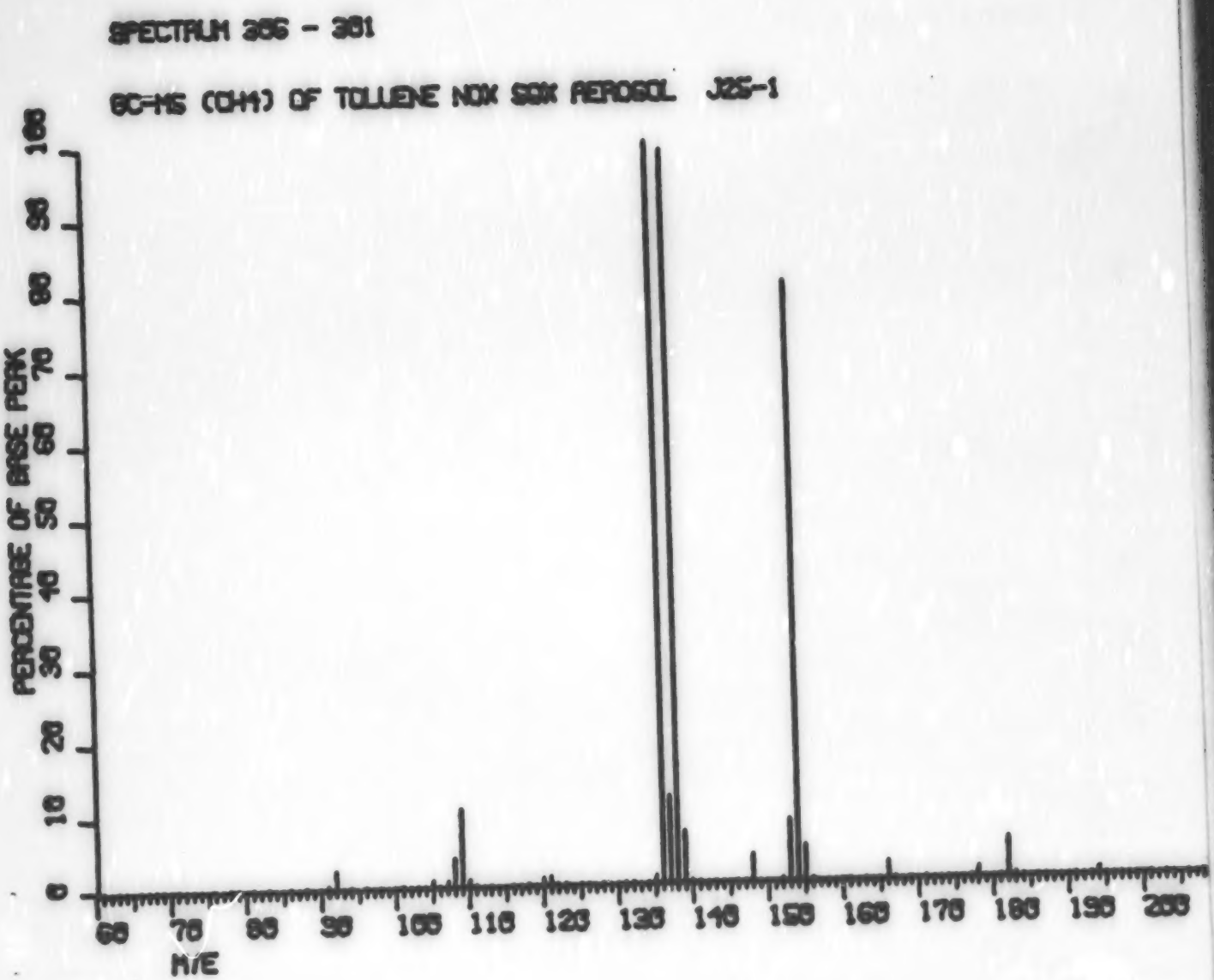


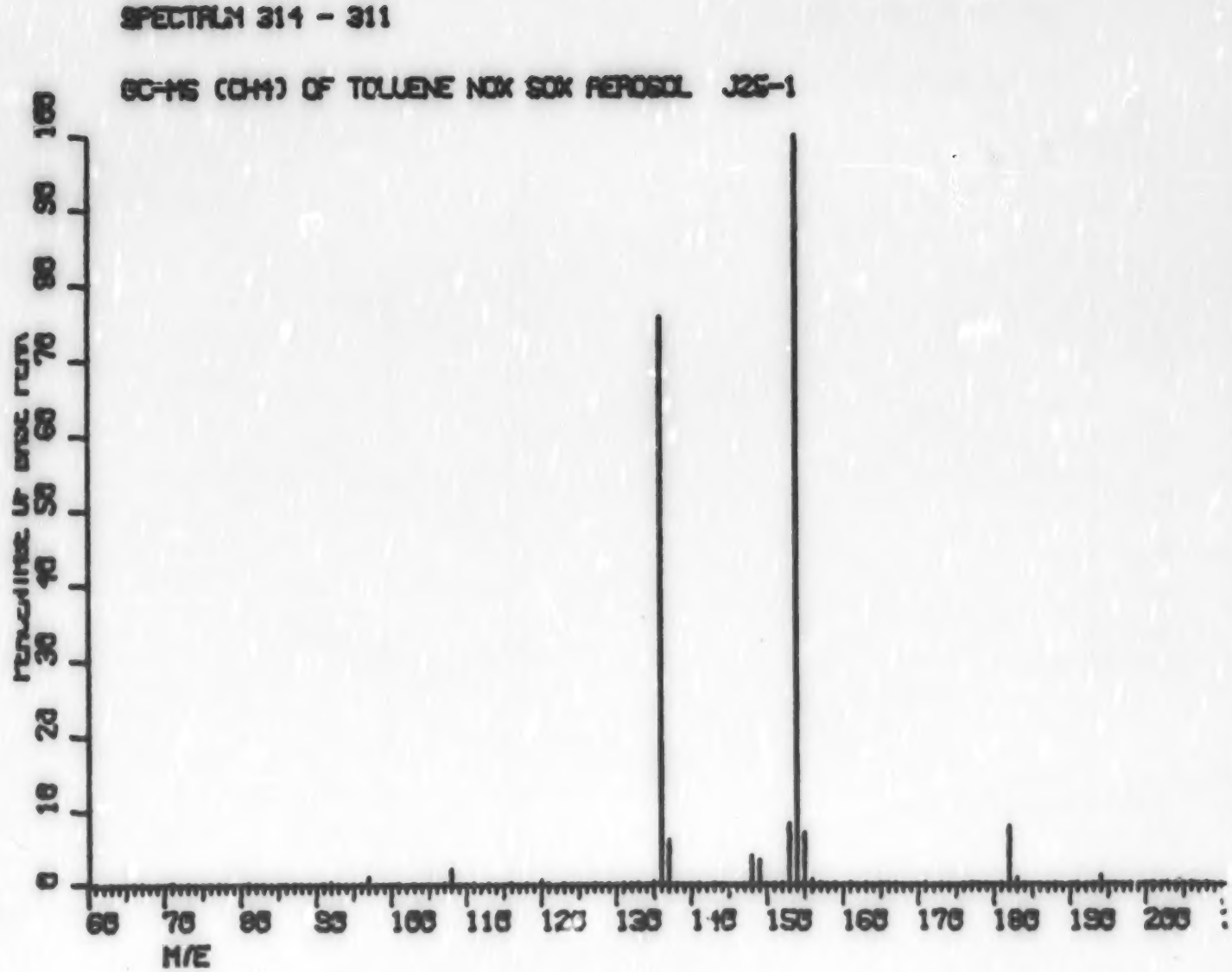

SPECTRUM 263 - 276
GC-MS (CH4) OF TOLUENE NOX SOX AEROSOL J25-1
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
M/E

SPECTRUM 282 - 287

GC-MS (CH4) OF TOLUENE NOX SOX AEROSOL J25-1

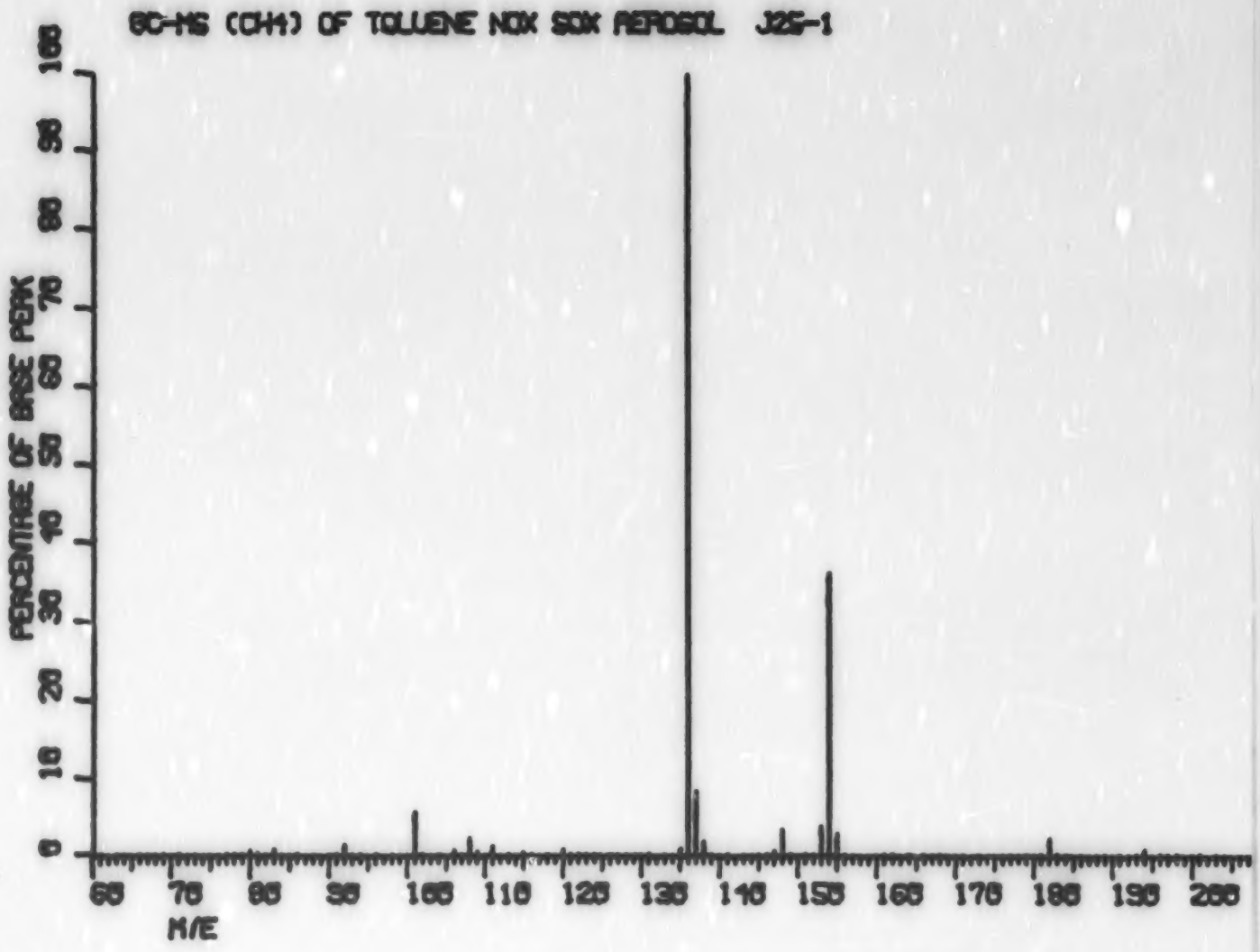



SPECTRUM 356 - 381
GC-MS (CH4) OF TOLUENE NOX SOX AEROSOL J25-1
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
M/E


SPECTRUM 314 - 311
GC-MS (CHM) OF TOLUENE NOX SOX AEROSOL J25-1
RUNNING MASS UP BASIC RUN
0
10
20
30
40
50
60
70
80
90
100
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
M/E

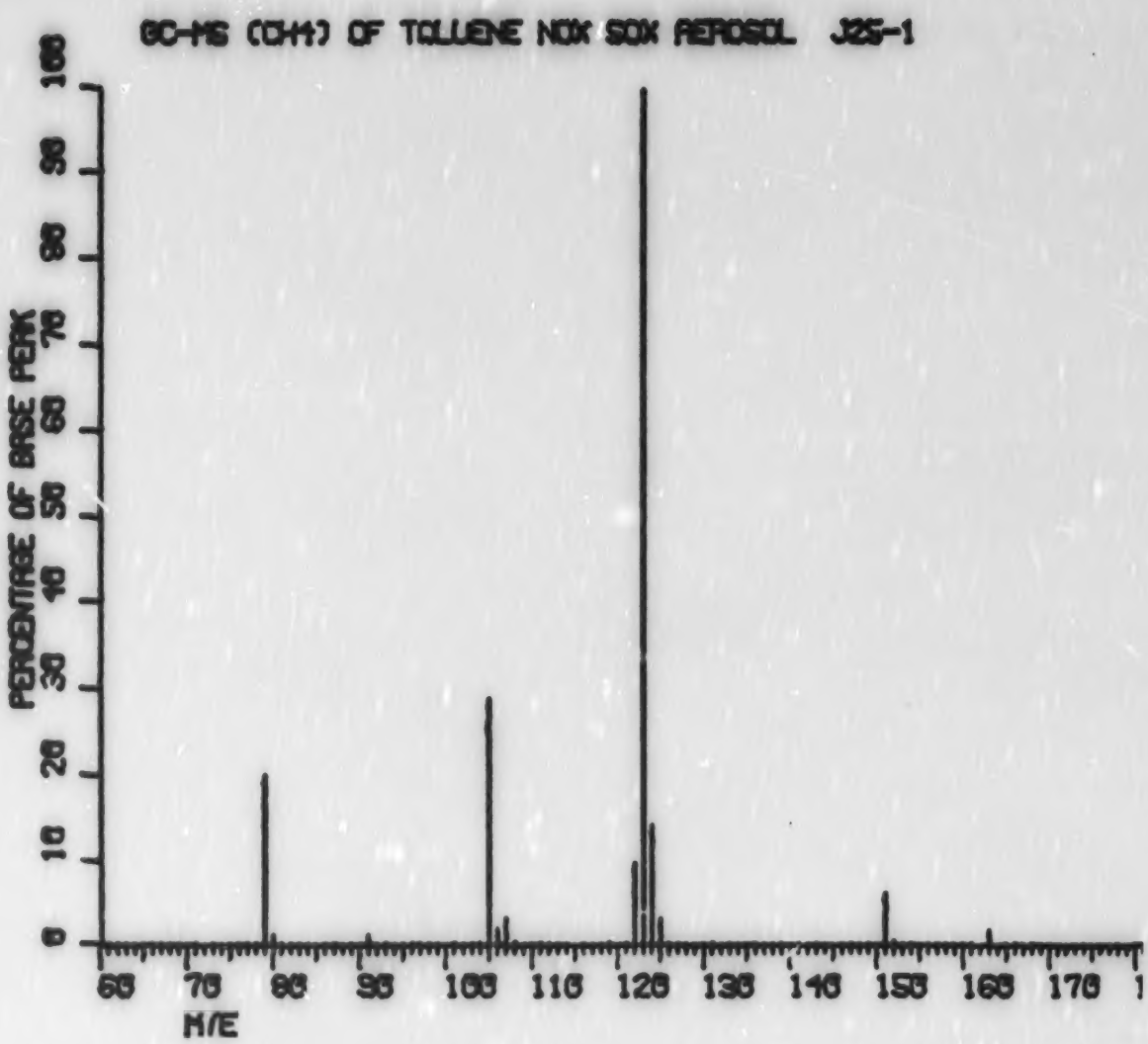
SPECTRUM 334 - 336

GC-MS (CH4) OF TOLUENE NOX SOX AEROSOL J25-1



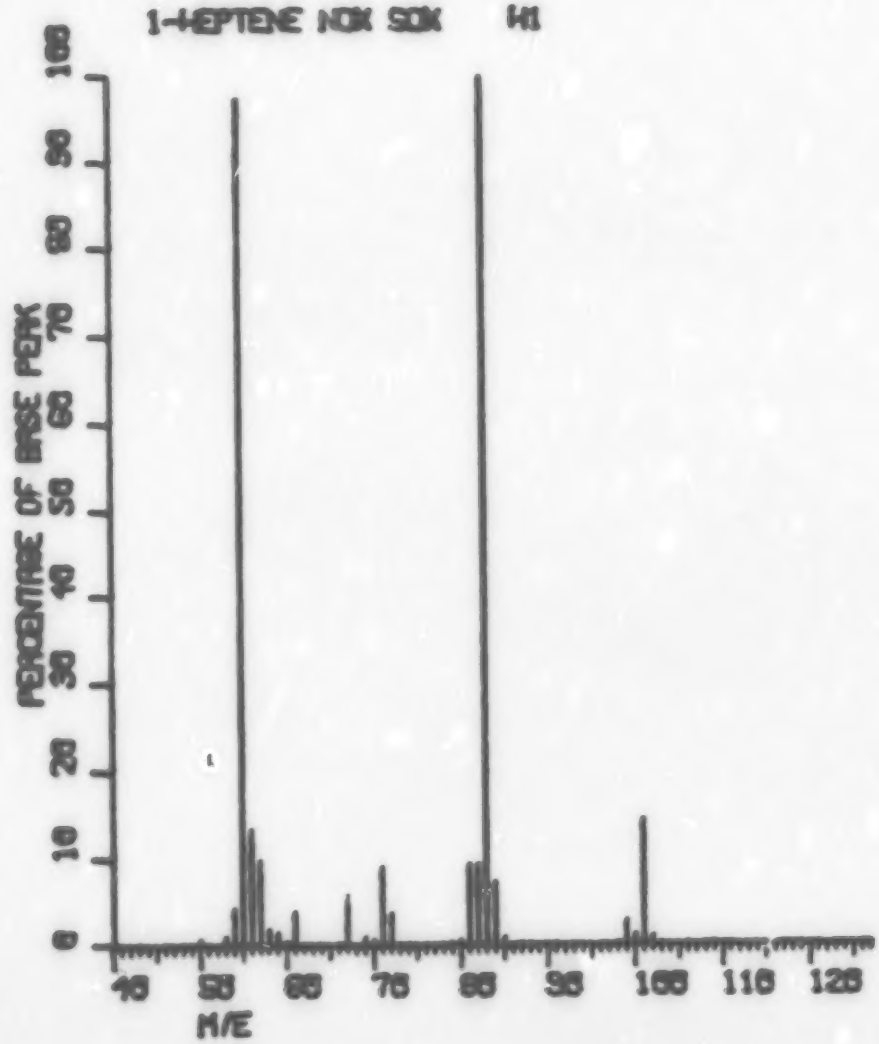
SPECTRUM 368 - 363

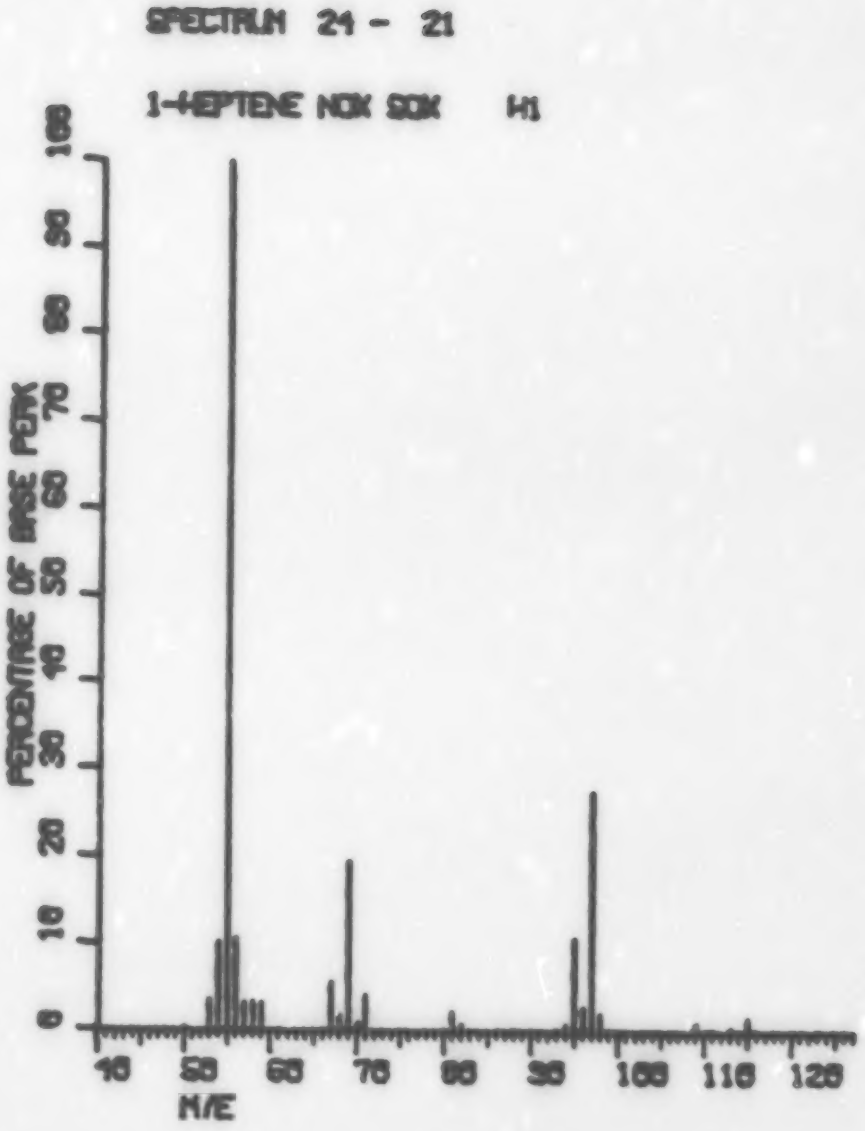
GC-MS (CH4) OF TOLUENE NOX SOX AEROSOL J25-1

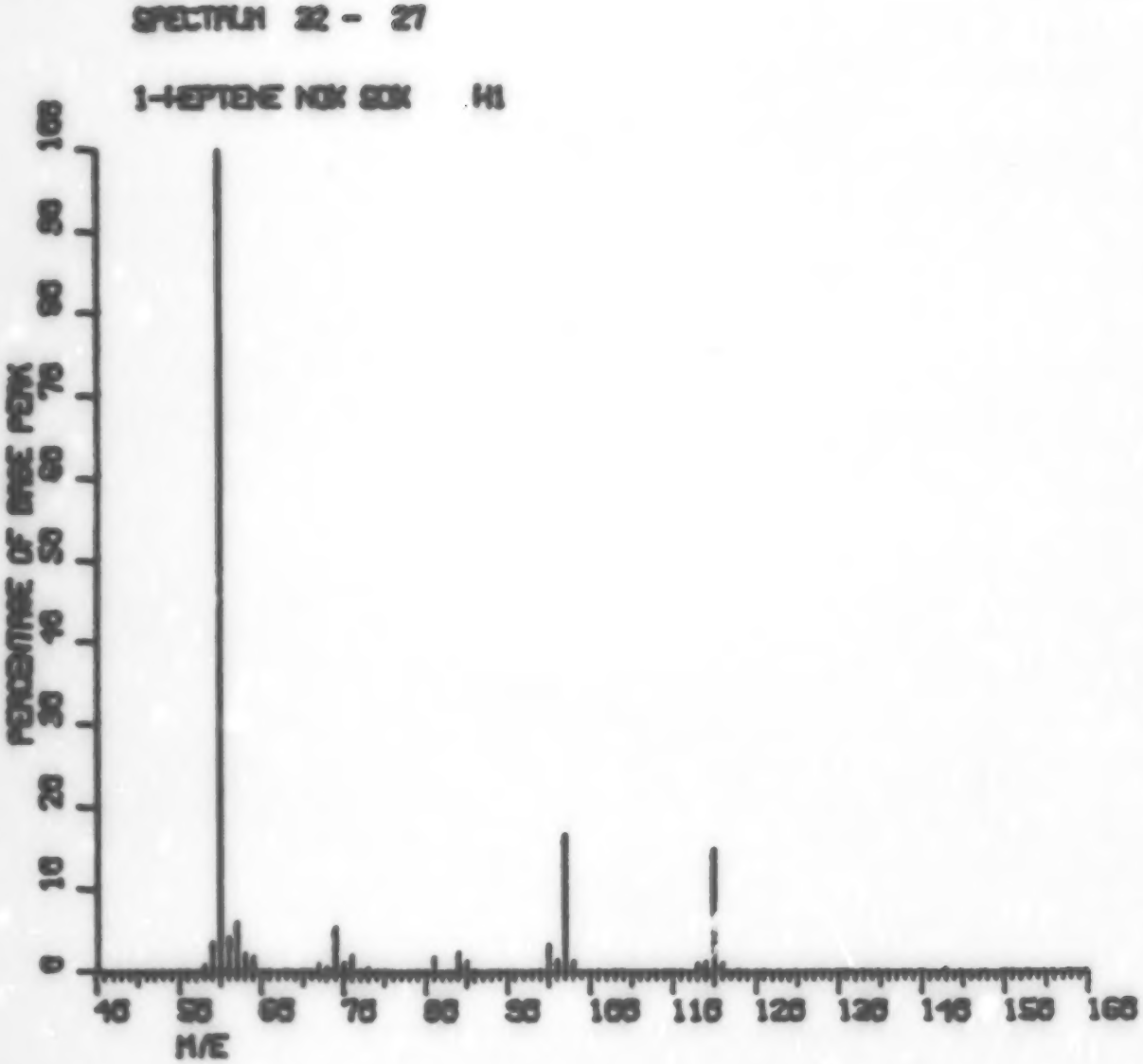


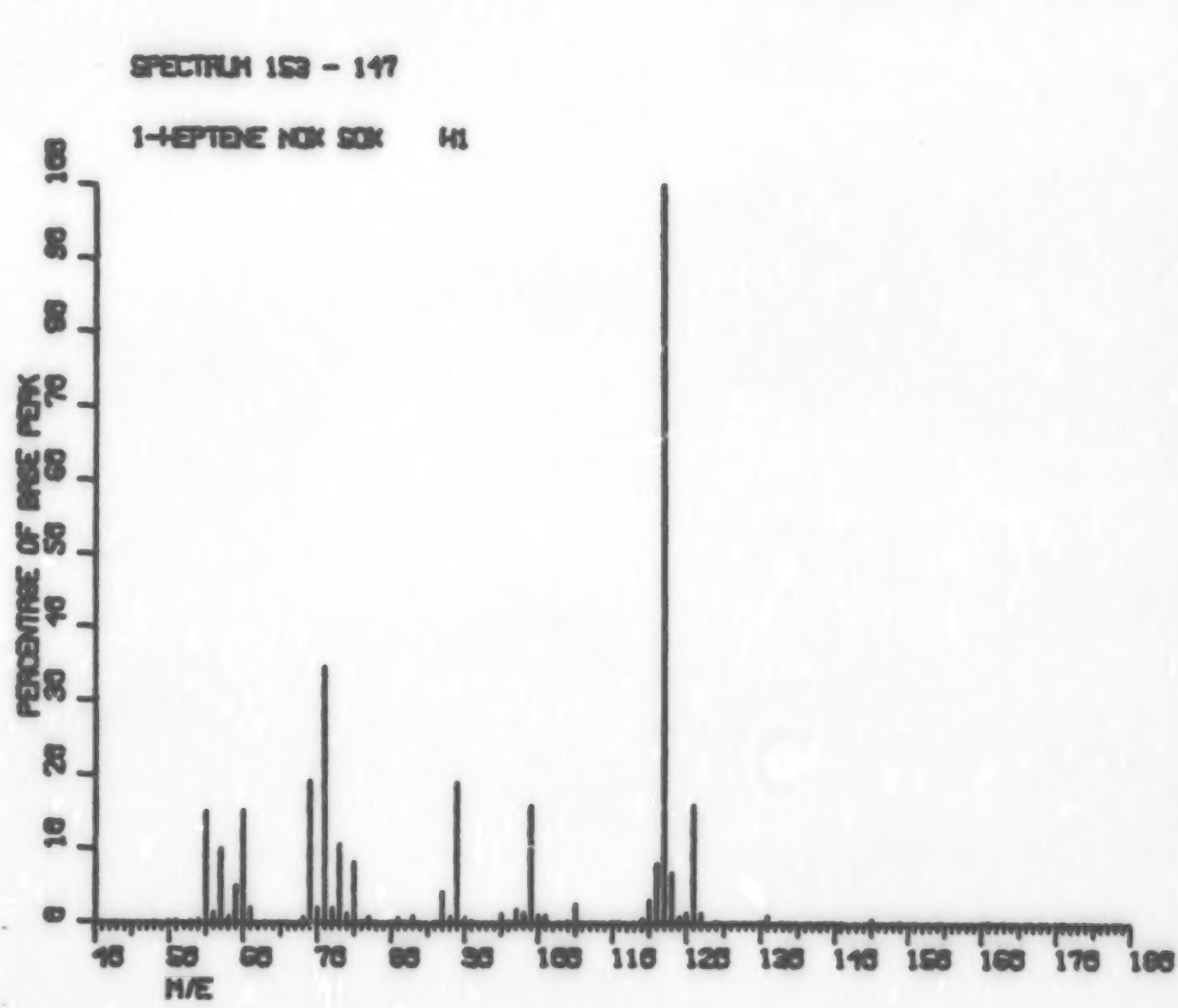
APPENDIX C

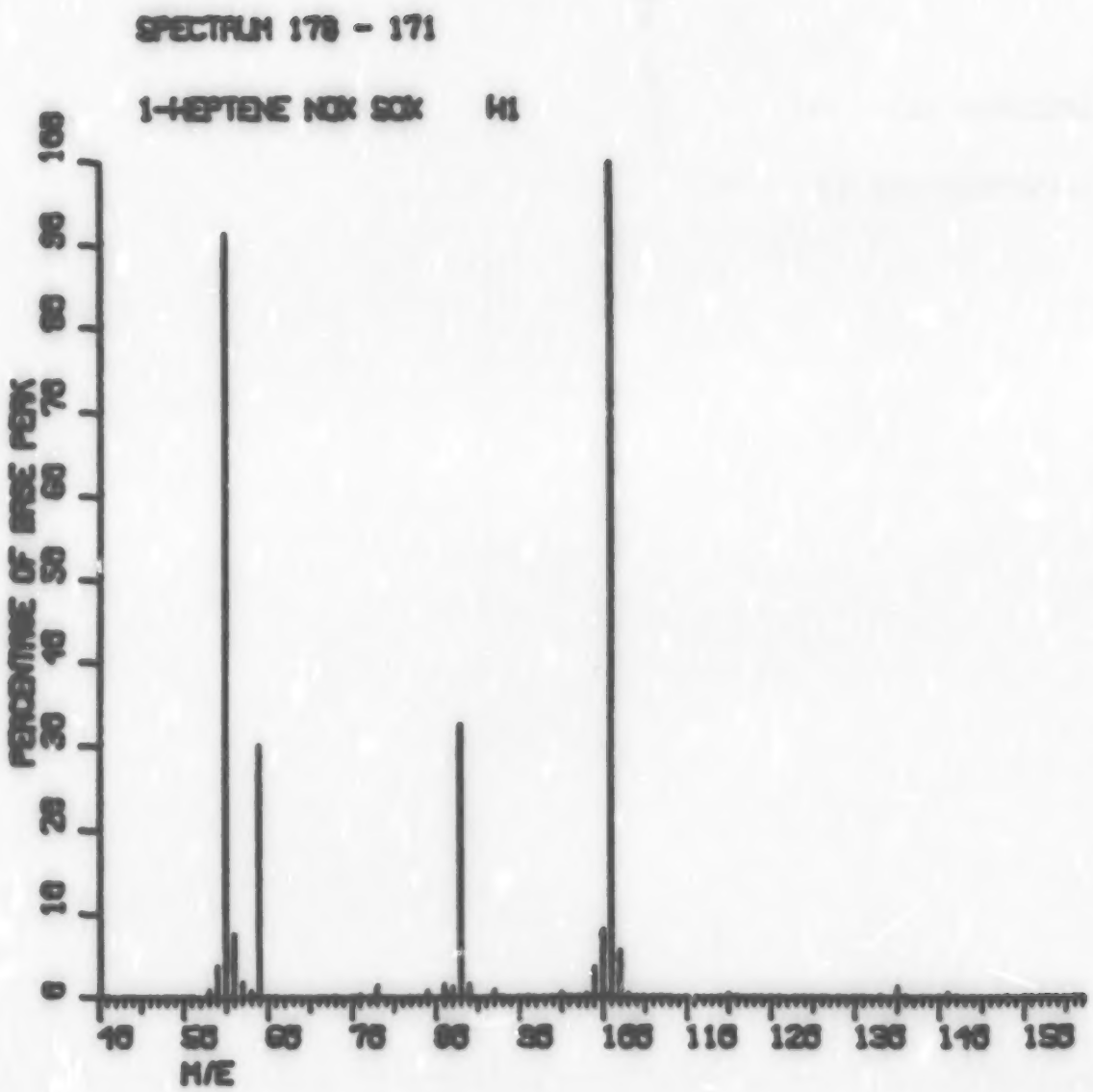
METHANE IONIZATION SPECTRA OF COMPOUNDS OBSERVED ON THE GC-MS ANALYSIS (FIGURE 16) OF VAPORS ASSOCIATED WITH 1-HEPTENE/NO_x/SO_2 AEROSOLS

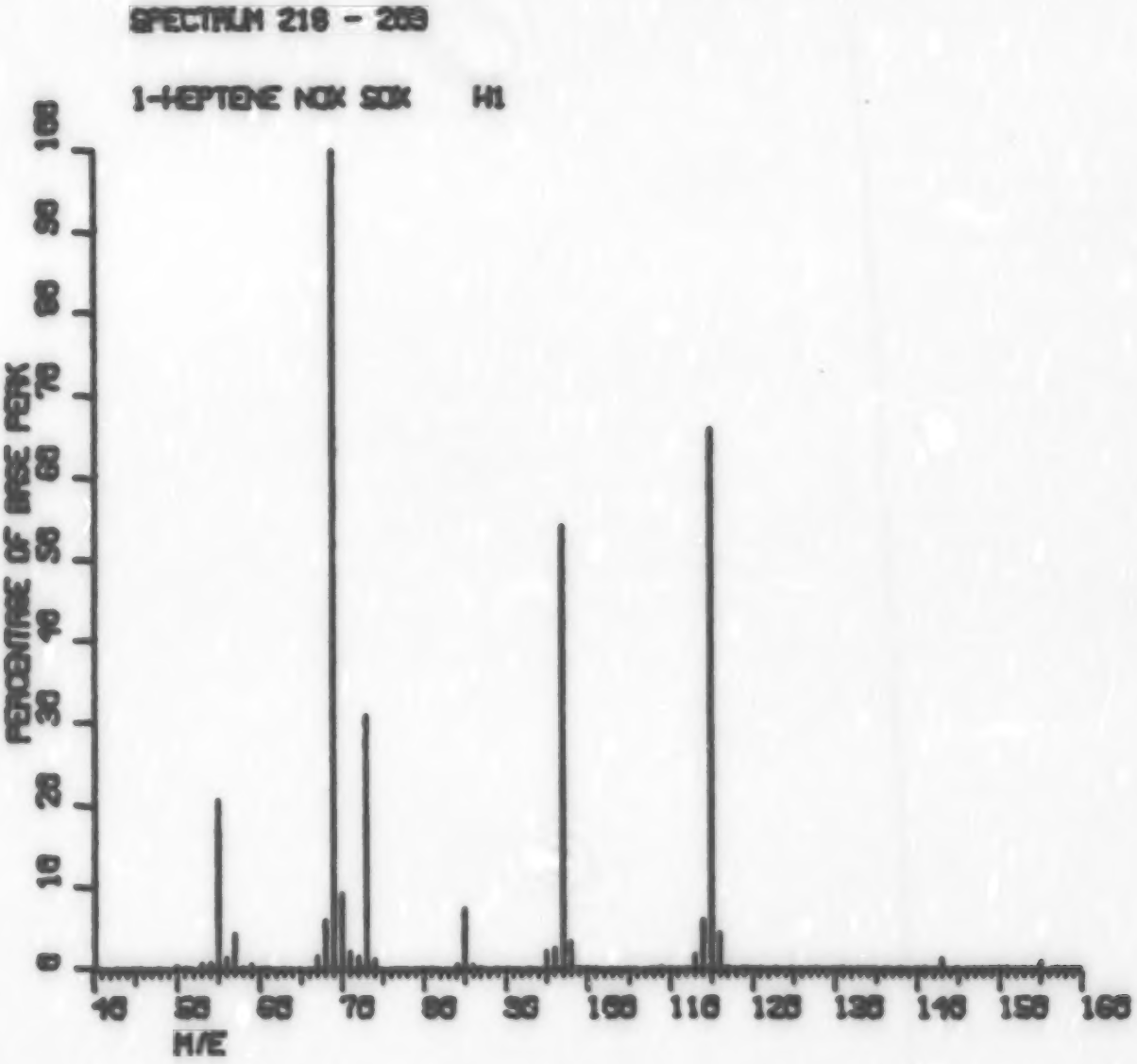

SPECTRUM 17 - 9
1-HEPTENE NOX SOX HI
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
40
50
60
70
80
90
100
110
120
M/E


SPECTRUM 24 - 21
1-HEPTENE NOX SOX H1
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
40
50
60
70
80
90
100
110
120
M/E


SPECTRUM 22 - 27
1-HEPTENE NOX SOX H1
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
40
50
60
70
80
90
100
110
120
130
140
150
160
M/E


SPECTRUM 153 - 147
1-HEPTENE NOX SOX H1
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
M/E
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180


SPECTRUM 170 - 171
1-HEPTENE NOX SOX HI
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
40
50
60
70
80
90
100
110
120
130
140
150
M/E


SPECTRUM 218 - 209
1-HEPTENE NOX SOX H1
PERCENTAGE OF BASE PEAK
0
10
20
30
40
50
60
70
80
90
100
40
50
60
70
80
90
100
110
120
130
140
150
160
M/E